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THE APPLICATION OF PHASE SELECTIVE ALTERNATING CURRENT POLAROGRAPHY TO THE ANALYSIS OF HEAVY METALS IN WATER

A THESIS

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THE APPLICATION OF PHASE SELECTIVE ALTERNATING CURRENT POLAROGRAPHY TO THE ANALYSIS OF HEAVY METALS IN WATER

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SUMMARY

The subject of this investigation has been the application of phase selective ac polarography and square-wave polarography to the analysis of heavy metals in water. Although both of these techniques were found to be suitable for water analysis, the majority of the study deals with the ac polarographic method due to unforeseen difficulties encountered in the construction of the square-wave polarograph. However, square-wave polarography did prove to be more sensitive than ac polarography. In addition, the square-wave technique was found to be more suitable for the analysis of species that are irreversible polarographically. In studies involving the reversible cadmium reduction and the irreversible zinc reduction in 1 F potassium chloride, the zinc response was better, with respect to the cadmium response, using square-wave polarography than ac polarography.

The theory of ac and conventional dc polarography is presented. In addition, advantages and disadvantages of ac and square-wave techniques as compared with conventional polarography are dealt with.

It has been found that the sensitivity of the ac polarographic instrument is such that the following metal ions can be detected down to a lower limit of about 10^{-6} formula weights per liter: Sb(III), Bi(III), Cd(II), Cu(II), In(III), Pb(II), Sn(II), Sn(IV), and Zn(II). In addition, Co(II), Ni(II), Mn(II), Tl(I), Fe(II), and Fe(III) can be analyzed down to a limit of approximately 10^{-5} formula weights per liter. Rather unsatisfactory results were obtained for Cr(III) and V(V) which could only be

detected down to about 10^{-4} formula weights per liter and all attempts to work with Al(III) failed.

The ac technique has proven to be very suitable for the analysis of multicomponent systems. A number of such systems is discussed in this study; particular attention is paid to metals which are normally difficult to simultaneously determine polarographically.

The presence of surfactants (surface-active substances) commonly interferes with the ac polarographic technique. The problems associated with various types of surfactants are presented. In addition, a standard procedure for the elimination of interferences caused by surfactants has been developed.

Finally, the results obtained from the analysis of some natural and industrial samples are reported.

CHAPTER I

THEORY

Heavy metals in water produce an undesirable taste in drinking water, are harmful to fish and other aquatic life, and if present in high enough concentrations, can be toxic to humans.

At the present time the methods used for the determination of metals in low concentrations in water are exceedingly time consuming and difficult. Large samples are required which then must be concentrated prior to rather involved chemical separations and subsequent determinations. The procedure for each metal ion is different and in some cases the separation procedures are not adequate and lead to erroneous results.

There is a need for an analytical technique which would allow the rapid and simultaneous determination of a variety of metals in water.

For many years classical (direct current) polarography has been used for the analysis of heavy metals in aqueous solutions but is seriously limited because its lower limit of detection is approximately 1×10^{-5} F. A further limitation is due to the problems encountered in the analysis of multicomponent systems since the current for each reduction step is added onto the current for all preceding reduction steps. Thus, for example, the current for the reduction of cadmium in small concentrations is essentially impossible to measure in the presence of the current due to a high concentration of lead.

Phase selective ac polarography and square-wave polarography are

recent modifications of classical polarography which greatly enhance the sensitivity and selectivity. The purpose of this project has been to investigate the suitability of these two techniques for the analysis of water for low concentrations of heavy metals.

Electrolysis

Electrolysis occurs when an external source of voltage is applied to an electrochemical cell to force a nonspontaneous electrochemical reaction to proceed. The electrodes connected to the positive and negative terminals of the voltage source are known as the anode and cathode, respectively. Oxidation proceeds at the anode, reduction at the cathode. The solution in the cell is known as the electrolyte solution or electrolyte.

Decomposition Voltage

Consider an experimental arrangement in which the electrolyte consists of a cation that can be readily reduced and an anion that can be readily oxidized. Two identical, inert (e.g. platinum) electrodes are dipped into the solution. The electrodes are connected through an external circuit to the negative and positive terminals of a voltage source and hence will be the cathode and anode, respectively.

If the voltage is applied to the cell and increased progressively, at first only a small rise in current is observed. During this time each electrode is said to be polarized, that is, no electrochemical transformation is taking place and, therefore, no continuous current can flow. At a certain voltage the current increases suddenly; the cation is reduced at the cathode and the anion is oxidized at the anode. The electrodes are now said to be depolarized since current is now passing through

the cell. The term polarization is used to describe any phenomenon that inhibits or limits current flow, while the term depolarization refers to a process that enables current to pass through the cell. Substances taking part in electrochemical reactions are called depolarizers because their presence causes the passage of current when the applied potential is sufficiently large.

When the current starts to flow, the voltage applied to the cell is sufficient to cause appreciable decomposition of the electrolyte and is then said to have reached the decomposition voltage. This voltage, as any across an electrochemical cell, consists of two portions: the anodic and cathodic decomposition potentials. Since there is some ambiguity in deciding when a current "just starts to flow," it is customary to define the decomposition voltage, E_d, as the zero current intercept obtained by back-extrapolation of the current versus applied voltage curve.

Back Electromotive Force

If the electrolysis current is allowed to flow for some time and then stopped, a voltage is found across the electrodes with the same polarities as during the electrolysis. This voltage arises within the cell, is in opposition to the applied voltage, and is known as the back electromotive force, or, the back emf. This back emf consists of two portions: the reversible back emf and the concentration overvoltage. The reversible back emf arises because a voltaic cell is formed when the electrolytic depositions took place and may be calculated from the Nernst equation.

For electrolysis to proceed the voltage applied to the cell must exceed the reversible emf of the voltaic cell that forms once electrolysis

is initiated. Commonly, the decomposition voltage is essentially identical to the reversible back emf. The reversible back emf, and consequently the decomposition voltage, increases as the concentrations of the relevant ions decrease. Since the concentrations of the ions continue to decrease as the electrolysis proceeds, the reversible back emf increases progressively.

IR Drop and Applied Voltage

The decomposition voltage, E_d, is in essence the applied voltage required to initiate electrolysis. In order to advance electrolysis at a reasonable rate, an additional voltage is required to overcome the electrical resistance of the cell. With an electrolysis current, I, the voltage required in excess over the decomposition voltage is given by Ohm's law: $E = IR$. If the cell resistance, R, is known, this voltage, called the IR drop, can be calculated. Consequently, the applied voltage, E_{app}, required to perform an electrolysis with the passage of a certain current may be given as: $E_{app} = E_d + IR$. However, this formula does not yet fully describe the situation.

Concentration Overvoltage

From the above, it would seem that once the decomposition voltage is reached, i.e., the electrode becomes depolarized, the current should increase in a linear fashion with the applied voltage. However, this is true only for a moderate voltage rise. At higher voltages, the current increase becomes progressively less than would correspond to a linear relation, and finally a point is reached beyond which an increase in applied voltage does not lead to any appreciable change in current, i.e. the electrode is again polarized. In order to explain this leveling of the

applied voltage versus current curve, a closer inspection of the electrode processes is necessary. Consider the situation in which a metal ion is deposited at the cathode. Since deposition occurs, the solution in the vicinity of the cathode becomes depleted of metal ions. Several processes operate to replace the metal ions that leave the solution as the electrolysis proceeds. Metal ions are transported to the electrode region by diffusion from the more concentrated solution. Other possible transport mechanisms are electrostatic attraction, convection, and agitation of the solution. As long as the applied voltage, and therefore the current, is not too large, the metal ions are replenished by these transport processes sufficiently fast. At higher voltages, however, the current cannot follow the voltage rise linearly because the ion transport lags. Finally a point is reached where the current is governed by the rate at which ions are transported to the electrode and a further increase in applied voltage no longer has any pronounced effect on the current.

The concentration overvoltage, E_{conc}, is related to the applied potential by:

$$E_{app} = E_d + IR + E_{conc} \qquad (1)$$

This additional voltage is appropriately termed the concentration overvoltage since it is caused by concentration effects. If the concentrations of the depolarizers immediately adjacent to the electrodes were known, then E_{conc} could be calculated using the Nernst equation. However, since these concentrations are not known, all that can be done is to neglect the concentration overvoltage and thereby obtain a minimum value for the applied voltage.

Kinetic Overvoltage

An additional type of overvoltage called kinetic overvoltage or activation overvoltage is frequently encountered, particularly when diatomic gases are produced in the electrode reaction. The mechanisms involved in the establishment of this overvoltage are complex and not fully understood.

For cases where no kinetic overpotentials are encountered the decomposition voltage equals essentially the reversible back emf, and can be calculated from standard electrode potentials and concentration data by means of the Nernst equation. When kinetic overpotentials are encountered, they must be considered in addition to the reversible back emf.

Denoting the kinetic overvoltage by the Greek letter eta, η, the relationship among the decomposition voltage, reversible back emf, and kinetic overvoltage may be given by:

$$E_d = E_{rev} + \eta \tag{2}$$

where both the decomposition voltage and the kinetic overvoltage consist of anodic and cathodic portions. Thus:

$$E_d = E_{d,a} - E_{d,c} \tag{3}$$

and

$$\eta = \eta_a - \eta_c \tag{4}$$

The anodic kinetic overpotential is always positive. It increases the magnitude of the anodic decomposition potential, $E_{d,a}$, and the decomposition voltage. The cathodic overpotential is always negative. It acts to

make the cathodic decomposition more negative, but it also increases the value of the decomposition voltage.

Thus for the anode:

$$E_{d,a} = E_a + \eta_a \quad (\eta_a \text{ is positive}) \tag{5}$$

and for the cathode

$$E_{d,c} = E_c + \eta_c \quad (\eta_c \text{ is negative}) \tag{6}$$

and by combining the appropriate expressions:

$$E_d = \overbrace{E_a - E_c}^{E_{rev}} + \overbrace{\eta_a - \eta_c}^{\eta} \tag{7}$$

The size of kinetic overpotentials depends on various factors. The electrode material and the nature of the electrode surface have a great influence. The exceptionally high kinetic overpotential of hydrogen on mercury is of great importance, since the wide applicability of the dropping mercury electrode (dme) in polarography stems in part from this phenomenon.

Classical Polarography

Assume that an electrolysis cell contains a cathode that is quite small in comparison to the anode. In such a case the concentration overpotential at the anode is negligible and the current is controlled by the cathodic concentration overpotential, which in turn is a function of the rate at which reducible species are transported to the cathode. If the small electrode were made the anode, the current would flow in the opposite

direction and would be controlled by the transport of oxidizable species. In either case, the current increases sharply once the decomposition potential of a given species is reached and later, due to the establishment of concentration overpotential, the applied voltage-current curve levels to a plateau. The current at the plateau is called the limiting current and is chiefly controlled by the rate at which the relevant reacting species reach the electrode.

If a solution is not stirred mechanically, the mechanisms that most commonly transport ions to the electrode are diffusion, electromigration, and convection. If migration and convection are made negligibly small, diffusion is the mechanism by which reducible species are transported to the cathode. Migration is rendered negligible by the presence of a relatively large concentration of an inert supporting electrolyte, whose ions serve to conduct current through the solution and thus dissipate the electrostatic force but are not reduced or oxidized over the range of potentials being studied. Convection is minimized by using an electrode which automatically renews itself, and the neighboring solution, before the diffusion layer has grown thick enough to cause convection currents. Such an electrode is the dropping mercury electrode which is described immediately below. Under these conditions, since the rate of diffusion is proportional to the concentration of the diffusing species, it is possible to establish a relationship between limiting current and concentration. It is these principles on which the method of polarography is based.

Early attempts to utilize the principles outlined above failed because solid electrodes were used. Distorted curves were obtained, which in addition were not reproducible because the shape strongly depended on

the history of the electrode. Although techniques using these electrodes have improved markedly in recent years, there remain many problems associated with their use for analytical purposes. In 1922 Heyrovský obtained reproducible results by employing a dropping mercury electrode (dme), i.e. a small electrode consisting of mercury drops formed at the immersed tip of a fine bore capillary. Since new drops are continuously forming during the experiment, reproducible results are readily obtained since each new drop has the same past history. This constantly renewable surface, along with the high hydrogen overvoltage previously mentioned, are two main advantages to the dme. Heyrovský named the technique polarography because it is based on polarization phenomena.

The classical polarographic experiment is performed by applying a direct voltage to a cell that consists of a dropping mercury electrode (which is polarized because of its small area) and an unpolarizable electrode. A large excess of supporting electrolyte that does not undergo an electrode reaction is added to essentially eliminate migration current as well as minimize the IR drop across the cell. The resulting current versus applied voltage curve is called a polarogram (Figure 1). The ascent in the curve is called the polarographic wave or step. The height from the base line (zero current) to the plateau corresponds to the limiting current. The limiting current under normal polarographic conditions is the sum of the residual current, i_{res}, and the diffusion current, i_{dif}. It is the diffusion current that is proportional to the concentration of the electrode-active species. The residual current must therefore be subtracted from the limiting current to obtain the desired diffusion current. The residual current results from the capacitive charging of the

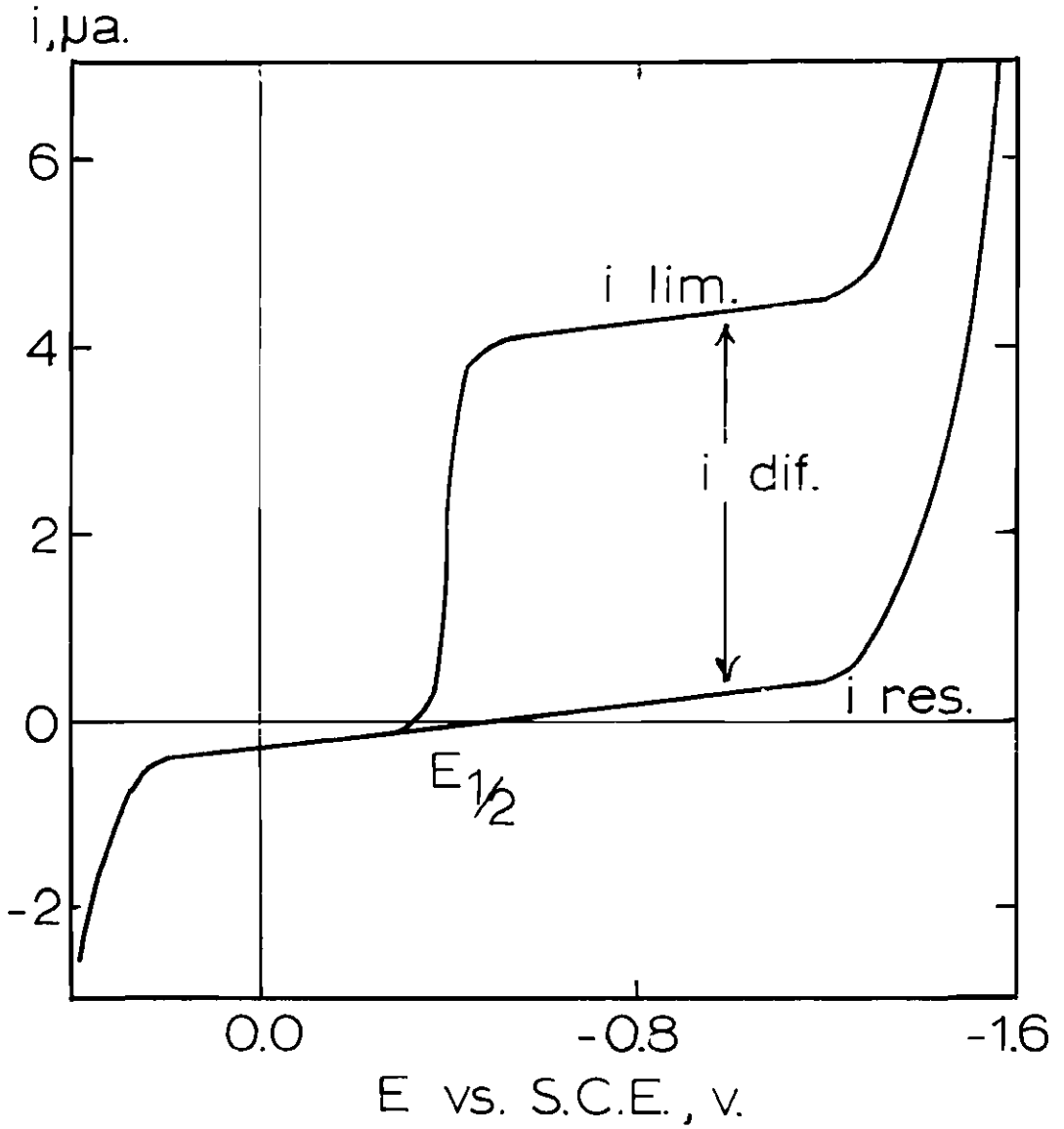

Figure 1. DC Polarographic Step

growing mercury drop and partially from the presence of polarographically active impurities in the solution. It is the presence of this residual current that greatly limits the detection limits of the classical polarographic method to about 10^{-5} formula weights per liter.

The half-wave potential, $E_{\frac{1}{2}}$ is the potential where $i = \frac{1}{2} i_{dif}$. It is characteristic of the electrode-active species and independent of the concentration of the species.

The Ilkovic Equation

The relationship between the diffusion current and parameters pertaining to the system under consideration has been derived by Ilkovic (using Fick's second law of diffusion and the appropriate assumptions) and the resulting equation is named after him:

$$i_{dif} = 607\ n\ CD^{\frac{1}{2}}\ m^{\frac{2}{3}} t^{\frac{1}{6}} \qquad (8)$$

Here i_{dif} is the average diffusion current in microamperes during the life of a drop, n the number of electrons transferred in the electrode reaction, C the concentration of the reacting species in millimoles per liter, and D the diffusion coefficient of the reacting species in square centimeters per second. The remaining two factors are characteristics of the capillary, m being the milligrams of mercury flowing from the capillary per second and t the drop time in seconds. The numerical factor 607 derives from some constants and conversion factors. This number would be 706 if the maximum current rather than the average current were being considered. From the equation it can be deduced that the diffusion current is proportional to the concentration of the reacting species if the parameters pertaining to the electrode are kept constant.

Multiple Polarographic Waves

A significant limitation to the classical polarographic method is that the half-wave potentials must differ by at least 0.15 volt in order for well separated waves to be obtained. When more than one reducible species is present in the solution, the resulting polarogram consists of successive steps due to the reduction of each species in turn. Such a situation is illustrated in Figure 2. Points A and B are the half-wave potentials of the two reducible substances with $i_{diff,A}$ and $i_{diff,B}$ being the corresponding diffusion currents. In order to obtain the diffusion current, it is necessary to measure the current from the base line of each individual wave, as is done with $i_{diff,B}$. The dashed line indicates the shape of the polarogram that would result if the substance B were absent. This additive nature of successive diffusion currents is one of the main limitations of classical polarography because it is frequently not possible to determine a reducible species in the presence of a relatively large amount of substance that is more easily reduced, i.e. reduced at a more positive potential.

Polarographic Reversibility

Polarographic steps are polarographically reversible when the current is controlled by the rate of diffusion of the depolarizer to the electrode surface. If any other factor controls the current the wave is not reversible. In addition to migration and convection mentioned above, factors capable of causing irreversibility are the following: adsorption phenomena at the electrode surface, a preceding slow chemical reaction, the effects of the diffuse double layer, and a slow electron transfer step. In order for the rate of an electron transfer step not to limit the current,

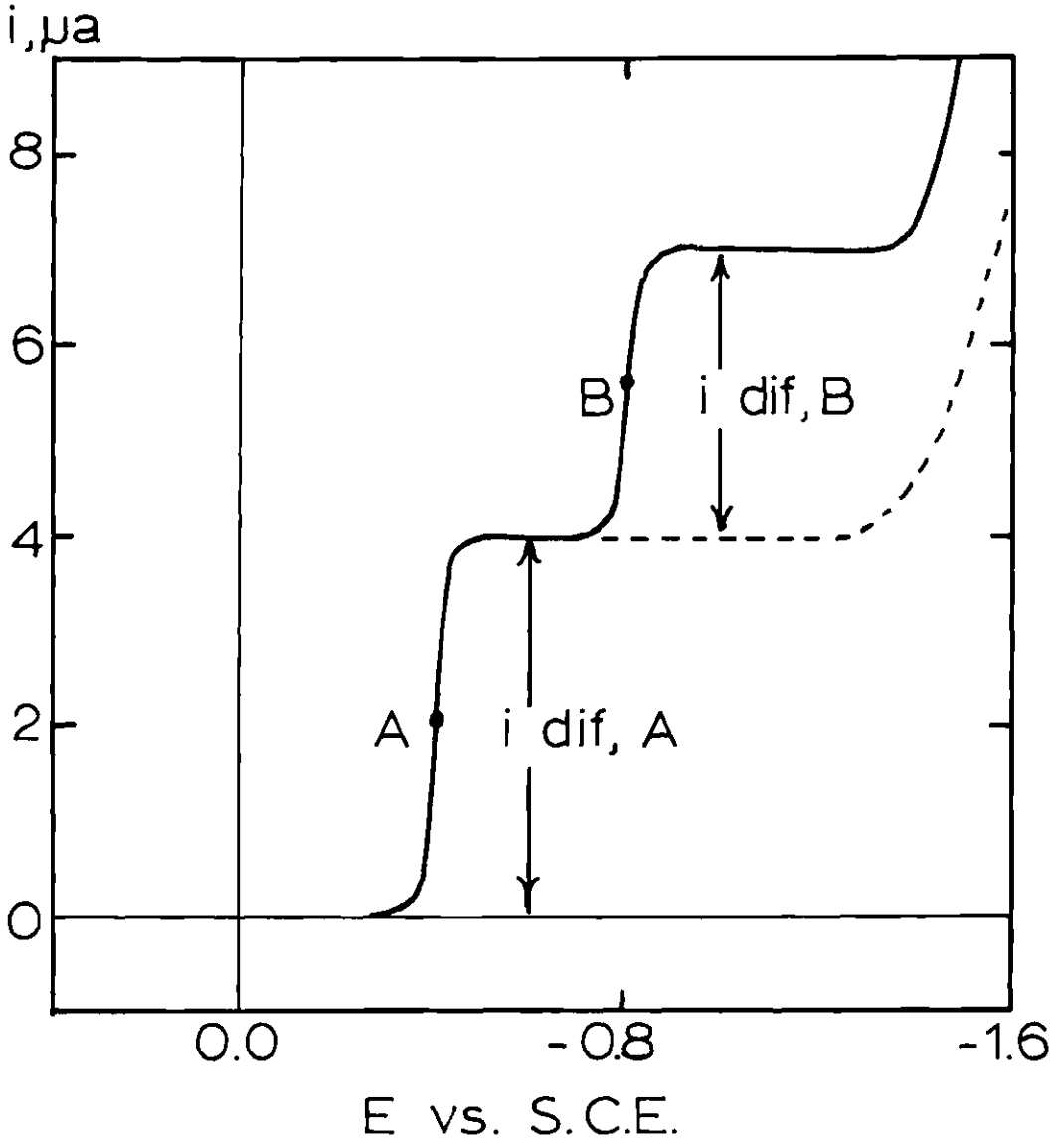

Figure 2. Multiple dc Polarographic Steps

the heterogeneous rate constant of the redox process must at least have a value of 2×10^{-2} cm sec^{-1} (1).

Hanging Mercury Drop Electrodes and Stripping Analysis

In addition to the dropping mercury electrode, stationary electrodes may be employed to obtain current-voltage curves. The most useful of these is the hanging mercury drop electrode.

A mercury drop may be hung onto a fine gold- or mercury-plated platinum wire sealed through, and barely protruding from the end of a glass tube. Other types employ syringe-type burets; by manipulation of a micrometer screw bearing on the plunger of the syringe, an accurately known volume of mercury may be forced out of a capillary to form a droplet on its tip. One of the latter types (available commercially) was employed in this study.

Although the dropping mercury electrode is more frequently used, because reproducible results are more readily obtained, the hanging mercury drop electrode offers some advantages over the dme (2). Among these advantages is the applicability of the hanging mercury drop electrode to techniques involving stripping analysis.

In conventional polarography one measures the limiting current arising from the forward (positive to negative) voltage sweep. As described above, the limiting current depends on the rate at which the depolarizer reaches the electrode and also includes the residual current. As the concentration of the depolarizer is decreased, the rate at which it reaches the electrode surface is also decreased, but the residual current remains the same. The residual current becomes a larger and larger part of the total current measured, and eventually the two become

indistinguishable.

If a depolarizer is deposited onto an electrode at a potential on the plateau of the wave or step, prolonged electrolysis at such a potential will cause the reduction or oxidation product to accumulate at the electrode surface. If the deposited substance can be reoxidized or rereduced, it will yield a correspondingly larger limiting current and the limit of detection is considerably improved. This is the principle of a family of techniques called stripping analysis.

Since the accumulation of material at the electrode surface is the basis of stripping analysis, the use of the dme is hardly possible. Stationary electrodes, including the hanging mercury drop electrode and solid electrodes of various materials are much more suitable.

The control of experimental variables is extremely important in stripping analysis. An accurate control and knowledge of the electrolysis (plating) time, T_p, is essential in order to correlate and reproduce results. Since most depositions are performed in stirred solutions, maintaining a uniform and controllable rate of stirring is necessary. Even when all experimental variables are carefully controlled, it is frequently difficult to obtain reproducible results.

Alternating Current Polarography

An increasing number of variations on the classical polarographic method has been developed over the years. Among these existing procedures is alternating current polarography.

The ac polarographic technique employs an alternating potential (of an amplitude small in comparison to the range of potentials usually

investigated) superposed onto the usual dc voltage. At values of direct potential where a redox reaction occurs, the effect of the superposed sinusoidal potential is to produce periodic concentration changes at the electrode-solution interface. These concentration changes are accompanied by periodic diffusion processes and the flow of alternating current. The current that arises due to the periodic redox reaction is called the faradaic alternating current.

The ac polarogram (Figure 3) is a plot of alternating current versus electrode potential. The faradaic alternating current only flows when both the oxidized and reduced forms of the depolarizer are present at the electrode surface; i.e. faradaic alternating current is only observed for potentials corresponding to the rising portion of the dc polarogram.

Terminology

To describe the characteristic features of an ac polarogram, Breyer (3) introduced the following terminology: Summit potential, E_s, the direct potential corresponding to the maximum alternating current; base current, the alternating current in the absence of a depolarizer; ac polarographic wave, the additional alternating current produced by the presence of a depolarizer. Breyer proposed to speak of ac polarographic waves and dc polarographic steps, a usage which will be followed in this report.

Advantages and Disadvantages

The ac polarogram appears to be (but is not) the derivative of the dc polarogram and has some advantages. Since the current returns to zero after each wave, better separation between closely spaced waves is obtained

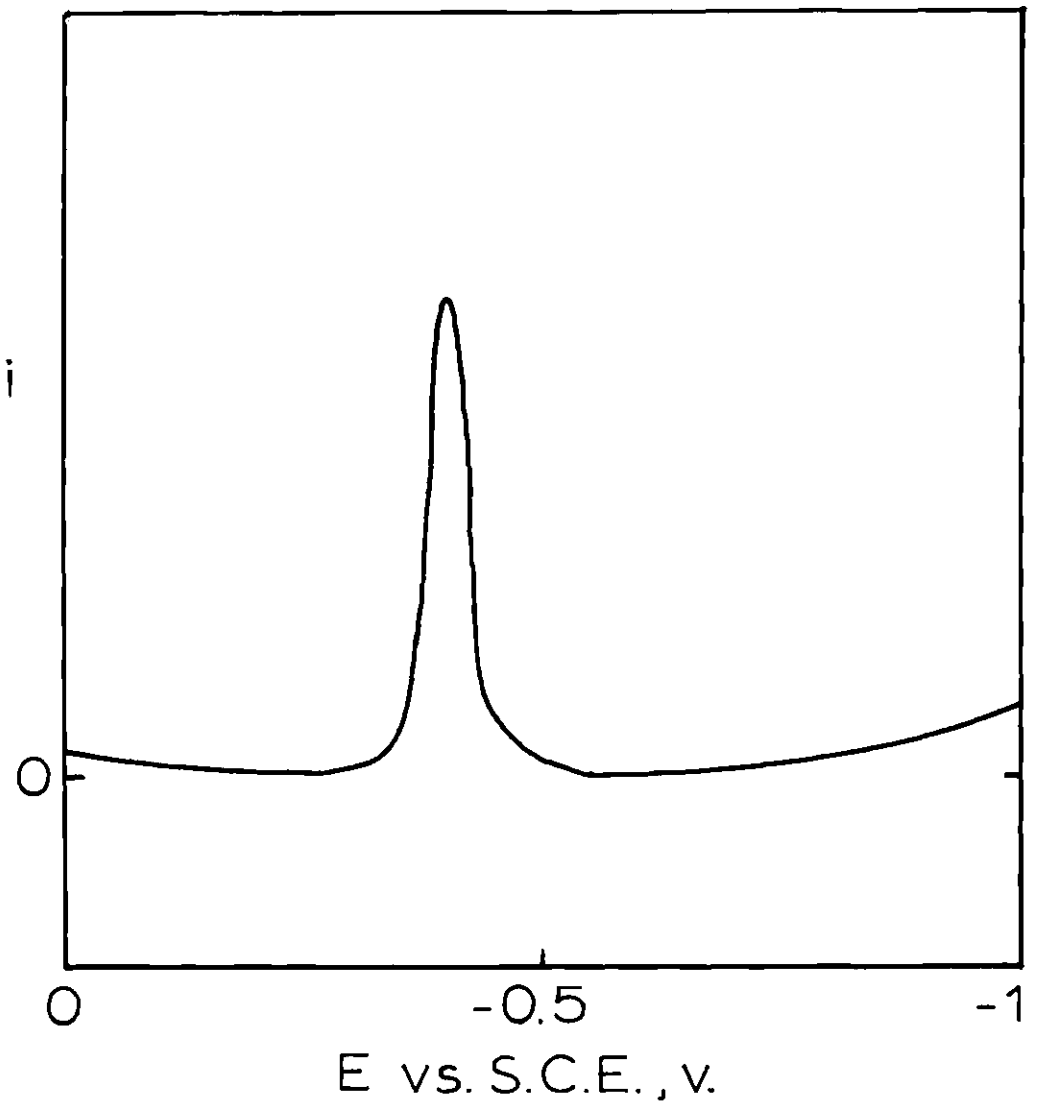

Figure 3. AC Polarographic Wave

and the peak height is measured from the zero current line for each wave. In addition to better separation, it is also possible to determine a reducible species in the presence of a relatively large amount of substance that is more easily reduced, i.e. reduced at more positive potential. This is frequently not possible with dc polarography due to the additive nature of the successive steps.

The ac method offers an additional advantage in that the kinetics of relatively fast redox reactions can be studied. The technique can be used for the measurement of rate constants, k, in the range of about 10^{-3} to about 1 cm sec^{-1}, and thus complements the dc polarographic technique which can give rate constant values only for quite irreversible processes ($k < 10^{-4}$ cm sec^{-1}). However, if the redox reaction is so slow that it is considered to be polarographically irreversible, then the ac technique will not yield a wave at all. This lack of applicability to irreversible processes is the main drawback to ac polarography.

Another disadvantage of the ac method is that it is not possible to distinguish between a reduction or oxidation process by looking at an ac polarographic wave, i.e. the appearance of the wave will be the same regardless of the ratio of the oxidized to reduced form of the depolarizer in the bulk of the solution. The dc steps are, however, in the case of reduction, cathodic (positive current) and in the case of oxidation, anodic (negative current).

Finally, the residual current for ac polarography is even larger than for dc polarography and thus no improvement in the detection limits is obtained. However, two modifications of ac polarography have been devised to minimize the residual current and thus improve the detection

limits of the method. These two modifications are square wave polarography and phase selective ac polarography (see below).

Effect of Frequency

An important parameter in ac polarography is the frequency of the superposed alternating potential. In discussing these implications, only the expressions for the cases of limitingly low and high frequencies, where the equations take particularly simple forms, will be given. While the terms "low" and "high" are only qualitative and depend upon the kinetics of the system being investigated, frequencies below 100 Hz may be considered low and frequencies above several thousand Hz may be considered high. At low frequencies the expression for the alternating current is:

$$\Delta i = \frac{n^2F^2AVC(\omega D)^{\frac{1}{2}} \exp P}{RT(d^{\frac{1}{2}} + \exp P)^2} \tag{9}$$

with the maximum value given by

$$\Delta i_s = \frac{n^2F^2AVC\ \omega^{\frac{1}{2}} D^{\frac{1}{2}}}{4\ RT} \tag{10}$$

and at high frequencies:

$$\Delta i = \frac{n^2F^2AVCk \exp [(1-\alpha)P]}{RT(d^{\frac{1}{2}} + \exp P)} \tag{11}$$

with the maximum value given by

$$\Delta i_s = \frac{n^2F^2AVCk(1-\alpha)^{1-\alpha}\alpha_o\alpha_d^{\alpha/2}}{RT} \tag{12}$$

where

n = number of electrons transferred per molecule of depolarizer

A = area of the electrode

V = amplitude of the superposed sinusoidal alternating voltage

C = bulk concentration of depolarizer

ω = angular frequency of the superposed alternating voltage

D = diffusion coefficient

$P = \frac{nFE}{RT}$; T = absolute temperature

k = heterogeneous rate constant of the redox process

α = transfer coefficient

d = ratio of diffusion coefficients of the oxidized and reduced species.

In the low frequency case, the periodic rate of the electrochemical reaction at the electrode-solution interface is much faster than the periodic diffusion changes, that is, $k >> (\omega D)^{\frac{1}{2}}$, and the current is governed by the frequency and is independent of the actual value of k. At high frequencies, where $k << (\omega D)^{\frac{1}{2}}$, the current depends directly on the magnitude of k and is independent of ω. From the above it can be deduced that it is better to operate at low frequencies when dealing with systems of borderline reversibility. In the low frequency case, the current increases linearly with $\omega^{\frac{1}{2}}$.

Width of the Wave at Half-Height

A useful way of characterizing the ac polarographic wave is by means of the width at half-height, $\Delta E_s/2$. This quantity can be obtained by finding the two potentials, $(\Delta E_s/2)_1$ and $(\Delta E_s/2)_2$, at which the faradaic alternating current is one-half of its maximum value.

At low frequencies, i.e. for reversible behavior, the width of the wave at half-height is given by

$$\Delta E_s/2 = \frac{RT}{nF} \ln \frac{3 + 2\sqrt{2}}{3 - 2\sqrt{2}} = \frac{90.5}{n} \text{ mv} \qquad (13)$$

This expression can readily be derived from equations 9 and 10.

This relationship is a very useful one in that a quick inspection of an ac polarogram enables one to ascertain the suitability of a particular polarographic reaction to the ac method, since any deviation from this criterion indicates an irreversible process.

The Summit Potential

The summit potential is, by definition, that potential at which the faradaic alternating current is a maximum. At low frequencies it is found to equal the classical polarographic half-wave potential for reversible systems, i.e. $E_s = E_{\frac{1}{2}}$. A deviation from this criterion also indicates irreversibility.

Phase Selection

As previously mentioned, phase selective ac polarography is one of the modifications of the ac technique that has improved the method.

This technique uses a phase selective detector which takes advantage of the phase differences between the faradaic current and the non-faradaic current arising from the capacitive charging of the electrode, i.e., the double-layer charging current.

The double-layer charging current is found to be 90° out of phase with the applied alternating potential; whereas, the faradaic current is 45° or less out of phase. By measuring only the current that is in phase

with the alternating potential, the phase selective detector essentially discriminates against the capacitance current and gives a reading that is a function of the faradaic current.

While conventional ac polarography and classical dc polarography have about the same detection limits, between 10^{-5} and 10^{-6} formula weights per liter, phase selective ac polarography has, in favorable cases, a detection limit below 10^{-7} formula weights per liter.

Of course, with detection limits this low the method is very susceptible to contaminants from a variety of sources: bubbler, tygon tubing, reagents, etc. With the ac technique one must be concerned with the purity of the mercury employed; whereas, the problem only arises in dc polarography when dealing with anodic processes, the mercury electrode may be a source of contamination for both cathodic and anodic reactions when using the ac technique due to the periodic oxidation-reduction process involved.

Square-Wave Polarography

This technique employs an alternating voltage of square-wave rather than sinusoidal shape superposed onto the usual dc voltage. Suppression of the double-layer charging current is achieved by using the fact that, after the application of a voltage-pulse to the electrode, the double-layer charging current decays more rapidly than the faradaic current. Thus, measurement of the current towards the end of the pulse leads to elimination of the double-layer charging current from the recorded polarogram.

In general, square-wave polarography is more suitable for the determination of systems involving irreversible polarographic reactions than the phase selective ac technique.

CHAPTER II

INSTRUMENTATION AND CHEMICALS

Polarograph

The phase selective ac polarograph used in this study is composed of a commercial lock-in amplifier (Princeton Applied Research model JB-4) as the signal source and phase-selective detector used in conjunction with a locally fabricated three electrode polarograph using solid state operational amplifiers and power supply (Philbrick models P65AU, P85AU, and PR 30). The circuit of the polarograph is basically very similar to that of the Heath EUW-401 polarograph, but is modified as necessary for the characteristics of the solid state amplifiers and also includes a positive feedback circuit to partially compensate for the IR drop in the cell. This latter feature is important in reducing the magnitude of the drop oscillations in the background current when using the dme. Thus the experimental setup is similar to that described by Evilia and Diefenderfer (4). Readout is obtained on a Hewlett-Packard 7004A X-Y recorder and a Dumont 304A oscilloscope is used to monitor the current output waveform and to aid in adjusting the lock-in amplifier.

A block diagram of the instrument is shown in Figure 4. Amplifier I is used to generate the slow ramp voltage used in both ac and dc polarography. Amplifier II is a voltage follower used to measure the potential of the reference electrode with respect to electrical ground, without drawing appreciable current from the electrode. Amplifier III is the control amplifier. This amplifier is actually used as a summing amplifier

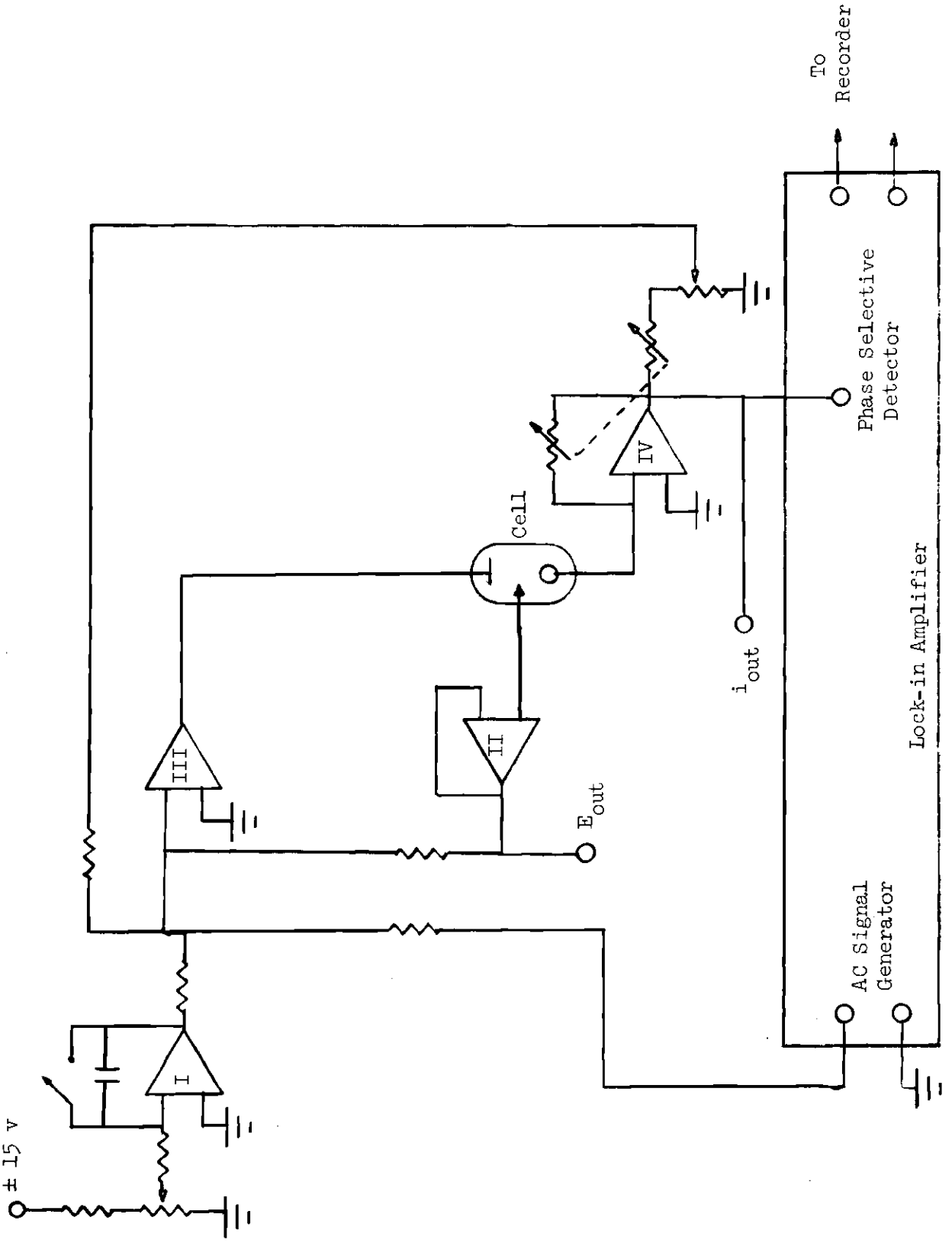

Figure 4. Block Diagram of the Instrument

in which the following signals are summed: the slow ramp voltage from amplifier I, the reference electrode potential from amplifier II, the initial potential, the ac signal generated in the PAR lock-in amplifier, and the positive feedback signal from amplifier IV. Amplifier IV serves as the current amplifier. The test electrode (i.e. the dme or hanging drop) is connected directly to the input of this amplifier and is thereby held at ground potential (virtual ground). Since the output voltage of amplifier IV is proportional to the cell current, a portion of this signal may be fed back to the input of amplifier III to partially compensate for the IR drop in the cell.

As mentioned above, the test electrode is held at ground potential. Thus the potential of the reference electrode with respect to ground is equal in magnitude but opposite in sign to the potential of the test electrode with respect to the reference electrode. This potential, available as the output of amplifier II, is used to drive the X axis of the recorder and is controlled by amplifier III so that it is equal to the sum of the ramp voltage, the initial potential, and the ac signal.

The output of amplifier IV may be used directly in dc polarography to drive the Y axis of the recorder or else may be divided down and dampened before such use. For ac polarography the output of amplifier IV is fed directly into the PAR lock-in amplifier. This amplifier, through use of a tuned circuit, selects only that portion of the total signal that is of the same ac frequency as the input ac signal, thus separating it from both direct current and other ac frequencies such as 60 cycle noise. Then a phase selective detector is used so that the output signal fed to the Y axis of the recorder is only that portion of the signal having the

desired phase relationship (i.e. approximately 45° shift from the applied signal).

The following voltage ramps (sweep rates) are available in either the cathodic or anodic directions; 0.5, 1.0, 2.5, 5.0, 10, and 25 millivolts per second. The full output voltage (10 volts) of the current amplifier (amplifier IV) can be set as equivalent to 2.0 microamperes to 5.0 millamperes in 11 steps (1-2-5 sequence). The initial potential control is a 10-turn potentiometer and a potential reversing toggle switch covering the range of ± 1.0 volt. The positive feedback control is a 10-turn potentiometer which can be set so as to compensate from 0 to 2.5 K ohms of IR drop.

The X-Y recorder is equipped with a 17171A dc preamplifier in the Y_1 position. This preamplifier has sensitivities of 0.5 millivolt per inch to 10 volts per inch in 14 steps (1-2-5 sequence). At first a 17170A dc coupler was used in the X_1 position giving a sensitivity of 0.1 volt per inch which is exactly the desired value. However, it was found, even with an applied ac signal of 4 millivolts peak to peak at 100 Hz, that the recorder responded to the ac signal and excessive wear of the slide wire was feared. Therefore the dc coupler was moved to the X_2 position and a locally fabricated active filter (low pass) with unity gain was installed in the X_1 position.

Cell

For most work, the cell was a 100 ml spoutless Berzelius beaker. At first a number 10 rubber stopper was drilled to accommodate the electrodes, nitrogen bubbler, etc. but later a Beckman 101253 beaker cap was

used. A medium porosity gas dispersion tube was used to disperse the nitrogen during deaeration.

Electrodes

The counter electrode was simply a short length of platinum wire sealed into a glass tube inside of which electrical connection is made to the lead from the polarograph.

The reference electrode was usually a Beckman 39170 fiber-junction calomel. In some experiments, using perchlorate as a supporting electrolyte, a double salt bridge system was necessary to prevent blocking of the salt bridge by a precipitate of potassium perchlorate. For these experiments a Coleman 3-710 calomel electrode was used in conjunction with a second 3-702 reservoir which contains the second (potassium free) electrolyte.

The dropping electrode, of conventional design, was locally fabricated. The hanging drop electrode was a Beckman 39016 which also serves as a sitting drop electrode when fitted with the alternate J-shaped capillary tube.

Chemicals

All chemicals employed were reagent grade material and, unless otherwise denoted, used without further treatment. J. T. Baker "Analyzed" Reagent Grade potassium nitrate, potassium chloride, potassium iodide, ammonium chloride, ammonium acetate, sodium chloride, sodium fluoride, potassium hydroxide, sodium hydroxide, potassium oxalate, sodium tartrate, sodium citrate, sodium succinate, potassium hydrogen phthalate, potassium thiocyanate, and potassium cyanide were used as supporting electrolytes.

In addition, Fisher Reagent Grade hydrochloric acid, nitric acid, and ammonium hydroxide were used. Allied Reagent Grade perchloric acid and Fisher Reagent Grade nitric acid were used in some studies as oxidants to obviate organic substances as well as supporting electrolytes.

Bethlehem Instruments triple-distilled pure mercury was used for most studies, Mallinckrodt Reagent Grade mercury was also used for the stripping analysis experiments.

Stock solutions 2.0 F in potassium chloride and 2.0 F in potassium nitrate were prepared and diluted as needed. Other stock solutions were prepared at values between 0.5 F and 1.0 F and diluted as needed.

Millimolar solutions of the following metal nitrates were prepared and diluted as needed; cadmium, cobalt, chromium, copper, lead, iron, manganese, nickel, and zinc. Millimolar solutions of antimony, bismuth, and tin were prepared by dissolving the metal-oxides in a minimum amount of hydrochloric acid per liter of water. Millimolar solutions of indium and thallium were prepared by dissolving the metal in acid and diluting to one liter.

Stock solutions 1.0 F in sodium hydroxide and 1.0 F nitric acid were prepared and kept in dropping bottles for pH adjustments. Standard buffers were used as pH standards.

A millimolar mercury(II) nitrate solution was prepared for studies involving a platinum electrode.

The detergents Tide X-K and Alconox were used in surfactant studies. Triton X-100, Armeen, Onyx, and sodium dodecylsulphate were also used for these studies.

Doubly deionized water was used exclusively.

Airco dry nitrogen was used for deaeration.

CHAPTER III

SIMPLE SYSTEMS

This chapter will include a systematic presentation of the applicability of phase selective ac polarography for the determination of individual metal ions in water. Each metal will be presented in alphabetical order with the optimum conditions for the determination being given. In addition, problems common to the determination of each species will be delat with.

It was found that the sensitivity of the instrument is such that the following metal ions can be determined down to a lower concentration limit of about 10^{-6} formula weights per liter: Sb(III), Bi(III), Cd(II), Cu(II), In(III), Pb(II), Sn(II), Sn(IV), and Zn(II). In addition, Co(II), Ni(II), Mn(II), Tl(I), Fe(II), and Fe(III) can be analyzed down to a limit of approximately 10^{-5} formula weights per liter. Rather unsatisfactory results were obtained with Cr(III) and V(V) which could only be detected down to about 10^{-4} formula weights per liter and all attempts to work with Al(III) failed. All summit potentials are presented with reference to the saturated calomel electrode.

Table 1 summarizes the results obtained for the determination of individual metal ions. In some cases, i.e. cadmium, lead, and thallium, a variety of supporting electrolytes were found to be equally suitable for analysis; in Table 1, however, only the data for one supporting electrolyte are given for each metal ion.

Table 1. Optimum Conditions for the Determination of Individual Metals

Metal Ion	Sb(III)	Bi(III)	Cd(II)	Cr(III)	Co(II)	Cu(II)
Most suitable supporting electrolyte	0.5 F hydrochloric acid	0.5 F hydrochloric acid	1 F potassium nitrate	saturated potassium bitartrate	1 F potassium thiocyanate	1 F potassium nitrate
Approximate detection limit	5×10^{-7} F (0.06 ppm)	3×10^{-6} F (0.6 ppm)	1×10^{-6} F (0.1 ppm)	1×10^{-4} F (5 ppm)	3×10^{-5} F (2 ppm)	5×10^{-6} F (0.3 ppm)
Reduction or oxidation product	Sb	Bi	Cd	Cr(II) and Cr	Co	Cu
Width of ac wave at half-height	30 mv	30 mv	45 mv	140 mv, Cr(III) → Cr(II) 50 mv, Cr(II) → Cr	90 mv	45 mv
Summit potential	-0.14 volt	-0.065 volt	-0.56 volt	-0.79 volt -1.1 volt	-1.1 volt	+0.03 volt

Table 1. Continued

Metal Ion	In(III)	Fe(III),Fe(II)	Pb(II)	Mn(II)	Ni(II)	Tl(I)
Most suitable supporting electrolyte	0.5 F hydrochloric acid	1 F potassium nitrate -0.1 F potassium oxalate, pH = 4	1 F potassium chloride	1 F potassium chloride	1 F potassium thiocyanate	1.0 F potassium chloride
Approximate detection limit	3×10^{-6} F (0.2 ppm)	5×10^{-6} F (0.3 ppm)	1×10^{-6} F (0.2 ppm)	2×10^{-5} F (1 ppm)	1×10^{-5} F (0.6 ppm)	1×10^{-5} F (2 ppm)
Reduction or oxidation product	In	Fe(II),Fe(III)	Pb	Mn	Ni	Tl
Width of ac wave at half-height	30 mv	90 mv	45 mv	60 mv	65 mv	90 mv
Summit potential	-0.60 volt	-0.23 volt	-0.43 volt	-1.48 volts	-0.71 volt	-0.49 volt

Table 1. Concluded

Metal Ion	Sn(IV) or Sn(II)	Zn(II)
Most suitable supporting electrolyte	1 F hydrochloric acid	0.01 F potassium chloride
Approximate detection limit	5×10^{-6} F (0.6 ppm)	1×10^{-6} F (0.06 ppm)
Reduction or oxidation product	Sn	Zn
Summit potential	-0.47 volt	-0.99 volt

Antimony

The method proved to be well suited to the determination of antimony in the +3 oxidation state. When present in the +5 state, antimony is not easily reduced and, therefore, reversible polarographic behavior is not observed.

A variety of supporting electrolytes was examined with a 0.5 F hydrochloric acid solution giving the best results. With this electrolyte a detection limit of about 5×10^{-7} F (0.06 ppm) and a summit potential, E_s, of -0.14 volt are obtained. The wave is perfectly symmetrical with a width at half-height of 30 mv which corresponds to the three electron change in the reduction of the species $HSbCl_4$ to elemental antimony.

An ac wave was not observed in the absence of a complexing agent. This is due to the irreversible reduction (5) of the "antimonyl" ion, SbO^+, which is the predominant species in the absence of a complexing agent.

In the presence of a non-complexing acid, such as nitric acid (1 F) no ac wave was obtained. This is in agreement with the fact that the reduction of SbO^+ does not proceed reversibly in nitric or sulfuric acid media (5). However, as chloride ions were added to the nitric acid system, an ac wave resulted, and the height of the wave increased progressively with increasing concentrations of chloride ions. This can be attributed to the formation of the reversibly reduced $HSbCl_4$ species. However, a supporting electrolyte of 0.5 F potassium chloride failed to give an ac wave for antimony. It appears that both a high chloride ion concentration and a strongly acidic solution are needed to form the reversibly reduced $HSbCl_4$ and obtain good results.

Chloride ion was the only unidentate complexing agent used.

Other complexing media, i.e. tartrate, citrate, and succinate were examined and results were obtained that are not completely satisfactory. A strong pH effect was observed and, in most cases, relatively broad doublets were obtained with a sensitivity much less than that of 0.5 F hydrochloric acid. Of these complexes, succinate proved to be the best; with a 0.5 F sodium succinate solution, pH adjusted to 4 with 1 F nitric acid, giving satisfactory results although the detection limit was only about 1×10^{-5} F (1 ppm) antimony. A single wave is obtained, with a width at half-height of 40 mv and a summit potential of -0.56 volt.

Although none of the above mentioned complexing agents gave results as good as hydrochloric acid, they could serve to verify the presence of antimony or to determine it in the presence of interfering species. In a 0.5 F hydrochloric acid solution Cu(II), E_s = -0.22 volt, may interfere with the determination of antimony if the concentration of copper is relatively high.

Bismuth

Bismuth is much like antimony in that a complexing agent is needed in order to obtain an ac polarographic wave. Again, an excellent wave was obtained in a supporting electrolyte of 0.5 F hydrochloric acid. This wave is narrow, width at half-height of 30 mv (corresponding to the three electron reduction of bismuth in the +3 oxidation state to elemental bismuth), has a summit potential of -0.065 volt, with a detection limit of about 3×10^{-6} F (0.6 ppm) bismuth. However, at low concentrations of bismuth the baseline in hydrochloric acid was uneven due to the dissolution of mercury: $Hg + 4Cl^- \rightleftarrows HgCl_4^{2-} + 2e$. This problem can be circumvented by lowering the chloride ion concentration in acid solution, even

though the bismuth wave is shifted to a more positive value. In a 1 F nitric acid solution that is also 0.05 F chloride ion, a symmetrical, well-developed wave is obtained with a summit potential of +0.01 volt. However, there is some loss in reversibility, the width of the wave at half-height is 55 mv, which is broad for a three electron change, and the detection limit is about 3×10^{-5} F (6 ppm) Bi; but the height of the wave is much easier to measure, at low concentrations, since the baseline is even.

Attempts to obtain an ac polarographic wave in a non-complexing acid, such as nitric acid, were not tried, but it is doubtful that suitable waves could be obtained under such conditions (6).

In a solution 1 F in both ammonium acetate and acetic acid a symmetrical wave with a summit potential at a relatively negative -0.2 volt was obtained. The dissolution of mercury does not cause an uneven baseline in this medium and the baseline is even. The width of the wave at the half-height is, however, relatively broad for a three electron reduction, 45 mv, and the detection limit is about 1×10^{-5} F (2 ppm) bismuth.

As was the case with antimony, the use of a variety of multidentate complexes has been explored. The summit potentials, detection limits, symmetry and narrowness of the waves were all found to be affected by the pH of the solutions. The best of these complexing solutions proved to be 0.1 F potassium hydrogen phthalate, with a pH of 4. In this electrolyte the dissolution of mercury is not a problem and a symmetrical, narrow (width at half-height of 35 mv) wave is obtained. The summit potential is -0.09 volt and the detection limit is about 5×10^{-6} F (1 ppm) bismuth.

A reasonably good wave is obtained using a supporting electrolyte of 0.5 F sodium succinate, pH = 4. A width at half-height of 45 mv is

obtained, with a summit potential of -0.15 volt, and a detection limit of about 1×10^{-5} F (2 ppm) bismuth. This would be a particularly good supporting electrolyte for the simultaneous determination of antimony and bismuth since the summit potential for antimony in this medium is -0.56 volt, a separation of 0.41 volt; whereas, the separation in 0.5 F hydrochloric acid is 0.075 volt. It is interesting to note that such separations are more critical when dealing with classical dc polarography than with the ac technique. At a higher pH value of 6.5, the bismuth wave is as good, E_s = -0.21 volt, but the antimony wave yields an ill defined doublet. Other multidentate ligands tried were citrate, oxalate, and tartrate. In general, relatively broad waves and/or uneven baselines were obtained using these complexing agents.

Because of its relatively positive summit potential in a variety of electrolytes, the ac polarographic technique is particularly well suited for the analysis of bismuth containing solutions since the current past the wave returns to the baseline. For this reason, the analysis of depolarizers that yield ac waves following the bismuth wave is usually easily accomplished, providing that the concentration of bismuth is not too large.

Cadmium

The polarographic reduction of the divalent cadmium ion to the metal is classically regarded as a reversible one. It is therefore not surprising that the cadmium gave a good ac polarographic wave in virtually every supporting electrolyte tried in this laboratory: potassium chloride, potassium nitrate, ammonium chloride-ammonium, potassium iodide, sodium

fluoride, potassium hydrogen phthalate, potassium thiocyanate, hydrochloric acid, perchloric acid, ammonium acetate-acetic acid, sodium citrate, and sodium oxalate. In most of these electrolytes cadmium gave a reversible wave with a width at half-height of 45 mv (corresponding to a two electron reduction); the detection limit was below 1×10^{-6} F (0.1 ppm) cadmium.

The only common polarographic interference of cadmium is the indium ion (see below).

In non-complexing media cadmium was found to be relatively unaffected by pH changes with consistent results being obtained in the pH range 3.0 to 7.5 using a solution that was 10^{-5} F cadmium ion. A 30 percent loss in height was found however when the pH was increased to 9.5. This is in rather sharp contrast to the lead ion which was drastically affected by pH changes (see below).

The use of a hanging mercury drop electrode for stripping analysis was employed to examine very small concentrations of cadmium. Using this technique detection limits below 1×10^{-8} F (0.001 ppm) cadmium could be realized. However, many problems were encountered using this technique and reproducible results were frequently difficult to obtain. As might be expected when dealing with such low concentrations, solutions were easily contaminated from a variety of sources, e.g., the bubbler, tygon tubing, etc. The supporting electrolyte (in this case potassium nitrate) had to be purified by electrolytic prereduction, although the amount of cadmium present was relatively small. An electrolytic prereduction simply involves removal of contaminants by electrolysis at a controlled potential; it proved to be reasonably effective providing the concentrations of con-

taminants were not too high; however, much time (between 10 and 15 hours) is required. The low cadmium contamination encountered could be obviated relatively easily using this technique.

When using the stripping technique, care must be taken to control experimental variables, such as plating time, uniformity of stirring, and size of the mercury drop.

Chromium

In general, rather poor results were obtained for chromium.

The most satisfactory ac polarographic behavior was obtained using a solution of saturated potassium bitartrate as a supporting electrolyte for the reduction of the chromium(III) ion. In this medium a doublet was obtained with summit potentials of -0.79 volt and -1.1 volts. The first wave corresponds to the reduction of chromium(III) to chromium(II) and has a width at half-height of 140 mv, which is quite broad for a one electron change. The second wave corresponds to the reduction of chromium(II) to the metal and has a width at half-height of 50 mv, and may therefore be considered a reversible two electron reduction. The detection limit in both cases was about 1×10^{-4} F (5 ppm) chromium. Narrower waves were obtained using a lower frequency of 24 Hz than the higher frequency of 100 Hz. This is in accordance with the theory outlined in Chapter II.

Attempts using other supporting electrolytes for chromium(III) proved to be futile. In the electrolytes, potassium chloride, potassium cyanide, sodium hydroxide, sodium citrate, and potassium oxalate chromium-(III) either gave very poor ac polarographic waves or no wave at all.

Cobalt

Cobalt is not well known for reversible polarographic behavior. However, reasonably good ac polarographic waves have been obtained in some supporting electrolytes.

Frequency studies using the cobalt(II) ion and a supporting electrolyte consisting of 1 F in both ammonium chloride and ammonia proved interesting. Using a frequency of 100 Hz and a cobalt(II) concentration of 7×10^{-5} F, a wave with a summit potential of -1.3 volts and a width at half-height of 100 mv (broad for a two electron change of Co(II) to elemental cobalt) was obtained. When the frequency was lowered to 24 Hz, a more narrow wave (width at half-height of 85 mv) was obtained. There was also a better signal to noise ratio at the lower frequency. Although the ac wave was still not reversible (width at half-height of 45 mv for a two electron change) there was a clear gain in reversibility at the lower frequency which is in accordance with theory. The detection limit in the ammonia medium at 100 Hz was about 4×10^{-5} F (2 ppm) cobalt(II) and was slightly better at 24 Hz.

In a supporting electrolyte 1 F in potassium thiocyanate a reasonably good wave at a potential of -1.09 volts was obtained with a width at half-height of 90 mv and a detection limit of about 3×10^{-5} F cobalt(II) (2 ppm). Although the baseline was uneven, the wave could be used for analytical purposes. In 0.5 F sodium fluoride a broad wave resulted (width at half-height of 210 mv) at -1.4 volts. The detection limit of about 1×10^{-4} (6 ppm) cobalt(II) was poor.

In the presence of ethylenediamine, both cobalt(II) and cobalt(III) gave good symmetrical waves in 0.1 F potassium nitrate at potentials

ranging from -0.39 to -0.47 volt (depending on the amount of ethylenediamine used). The width at half-height was about 90 mv (corresponding to the one electron reduction or oxidation for the Co(II)-Co(III) couple); the detection limit was about 5×10^{-5} F cobalt. This is an excellent medium for the determination of cobalt.

Copper

The method proved to be well suited for the determination of copper ions. In a non-complexing medium, such as potassium nitrate, a wave is obtained at +0.03 volt which corresponds to the two electron reduction of copper(II) to the metal. A width at half-height of 45 mv is found indicating that the reduction is reversible. The detection limit is about 5×10^{-6} (0.3 ppm) copper. The wave does suffer in terms of analytical application in that the baseline is uneven due to the wave caused by the anodic dissolution of mercury immediately preceding the copper wave. However, this is not a problem at copper concentrations well above the detection limits.

In a solution of potassium chloride the situation is quite different. In this medium, at a potential of +0.04 volt, copper(II) is reduced to copper(I), which is stabilized by the chloride ion. At low concentrations of copper this reduction is masked completely by the anodic dissolution of mercury which is shifted to more negative potentials by the presence of chloride: $Hg + 4Cl^- \rightleftarrows HgCl_4^{2-} + 2e$. Copper(I) is then reduced to the metal at a potential of -0.23 volt which gives rise to a symmetrical wave with a width at half-height of 80 mv indicating a reversible one electron reduction. The wave is well suited for the determination of copper; the

detection limit, 1×10^{-5} (0.6 ppm) copper, is not as good as that in potassium nitrate, but a more even baseline is observed.

A supporting electrolyte 1 F in both ammonia and ammonium chloride gave a wave much like that obtained in potassium chloride except that an uneven baseline was caused by the shifting of the wave, corresponding to mercury dissolution, to more negative potentials as a result of the mercury-ammonia complex formation.

The determination of copper using a supporting electrolyte of potassium hydrogen phthalate using frequencies of 100 and 24 Hz is noteworthy. Although the dissolution of mercury caused an uneven baseline at both frequencies, the problem was much less severe at 24 Hz. This phenomenon was also noticed in other cases where mercury dissolution was a problem; i.e., a lower frequency sometimes allowed a better separation from the mercury dissolution wave.

Attempts to determine copper using stripping analysis were unsuccessful due to a relatively high amount of copper in the available mercury. No attempts were made to purify the mercury.

Indium

It was found that the reduction of the indium(III) ion produced well defined ac polarographic waves in supporting electrolytes of hydrochloric acid, potassium chloride, ammonium acetate-acetic acid, sodium citrate, potassium hydrogen phthalate, and potassium iodide. These waves are all narrow with a width at half-height of about 30 mv (indicating a reversible three electron reduction), the detection limit is about 3×10^{-6} F (0.2 ppm) indium ion.

The reduction in potassium iodide is particularly important because it makes the simultaneous determination of indium and cadmium feasible. At 100 Hz the ac wave due to the dissolution of mercury was found to cause an uneven baseline; whereas, at 24 Hz this problem was eliminated.

Cadmium is the only metal ion that interferes with the determination of indium; and, while indium is easily rendered nonreducible in the presence of cadmium, the reverse situation is not readily attainable. The simultaneous determination of cadmium and indium will be discussed in the next chapter.

Iron

The presence of an appropriate complexing agent is necessary in order to obtain an ac polarographic wave for iron. In the presence of oxalate and citrate well defined ac waves were obtained under proper conditions.

As expected, waves obtained with the respective iron complexes were found to be dependent on pH.

In a supporting electrolyte, 0.1 F in potassium oxalate and 1 F in potassium nitrate with the pH adjusted to 4, a very well defined wave at a potential of -0.23 volt was obtained. The width of the wave at the half-height was 90 mv indicating a reversible wave for the one electron redox reaction of the iron(III)-iron(II) couple. The detection limit was about 5×10^{-6} F (0.3 ppm) iron. As expected, the appearance of the ac polarogram was the same for the reduction of iron(III) and for the oxidation of iron(II).

Initially a solution containing only potassium oxalate was used.

While a well defined wave was obtained, the background current was high. This problem was solved by holding the concentration of potassium oxalate at 0.1 F, but making the solution 1.0 F in potassium nitrate. The potassium nitrate apparently served to minimize the double-layer charging current and thereby lowered the background. Similar results were obtained employing citrate as a complexing agent, with best results being obtained with a solution 0.5 F in sodium citrate and 1 F in potassium nitrate at a pH of 4. Using this system, a well defined iron wave was obtained with a potential of -0.09 volt, a width at half-height of 90 mv (indicating a reversible redox reaction for a one electron change), and a detection limit of about 1×10^{-5} F (0.6 ppm) iron.

When using the oxalate system to analyze for iron in natural waters it was observed that sometimes a white precipitate of calcium oxalate formed. In order to ascertain whether or not the iron determination was affected by the presence of this precipitate, two identical solutions 1.0×10^{-5} F in iron were prepared except that one was made millimolar in calcium ion (this amount gave much more precipitate than any of the natural water samples). The two solutions were analyzed for iron using the potassium oxalate-potassium nitrate electrolyte. Identical results were obtained indicating that the presence of rather high concentrations of calcium in the original sample do not affect the determination.

Lead

The reversible polarographic behavior of the lead ion is well known and a well defined ac wave was obtained for this metal ion in virtually every supporting electrolyte tried: potassium nitrate, potassium chloride,

potassium hydroxide, hydrochloric acid, perchloric acid, ammonium chloride, ammonia-ammonium chloride, potassium hydrogen phthalate, sodium citrate, sodium succinate, acetic acid-ammonium acetate, and potassium oxalate. The summit potentials ranged from about -0.39 volt in potassium nitrate to -0.76 volt in potassium hydroxide. Most of the waves had a width at half-height of 45 mv indicating reversible behavior for the two electron reduction of lead(II) to the metal.

Results obtained using the hanging mercury drop for stripping analysis were much the same as those found for cadmium. A detection limit at about 1×10^{-8} F lead was realized under ideal conditions. The contamination of reagents by lead was much more of a problem than with cadmium. Both of the contaminants could be removed by electrolytic prereduction (see cadmium), but the removal of lead required a much higher electrolysis time, exceeding 20 hours. The mercury initially used for these studies (Bethlehem Instruments triple-distilled mercury) contained unacceptable amounts of lead for studies involving concentrations below 1×10^{-6} F lead. However, reagent grade mercury from Mallinckrodt was found to be acceptable for these studies.

In addition to the conventional type of stripping analysis using the hanging mercury drop electrode, some work was done using a mercury coated rotating platinum electrode. Work with electrodes of this type has been reported in the literature (7,8,9).

It was felt that the mercury coated rotating platinum electrode would offer the advantage of the high hydrogen overpotential commonly associated with the mercury electrode as well as eliminate the possible loss of the electro-active species (in this case lead) by diffusion into the

mercury drop.

The mercury was plated onto the rotating platinum electrode (E. H. Sargent and Co., type KYC-22, 1800 rpm) by holding the potential of the electrode at 0.0 volt in a stirred solution 0.1 F in nitric acid and 5×10^{-4} F in mercury(II) for 15 minutes. Once this process was completed the lead was deposited onto the mercury coated platinum electrode followed by anodic stripping. This procedure, i.e., first coating the platinum electrode with mercury and then depositing the lead, was found to be superior to the simultaneous deposition of the two metals; although Bruckenstein and Nagai (7) have reported the simultaneous deposition of thallium(I), lead(II), and mercury(II) ions onto platinum in similar solutions at potentials as negative as -1.05 volts.

In general, the mercury coated platinum electrode resulted in poor reproducibility. It was possible to achieve a detection limit of about 1×10^{-8} F lead which offered no improvement over stripping analysis using the hanging mercury drop. Since the results were more reproducible using the hanging mercury drop, it was judged superior for stripping analysis.

In non-complexing media, the ac wave of lead was found to be rather strongly affected by pH changes. In a supporting electrolyte 1.0 F in potassium nitrate 1×10^{-5} F lead gave an ac polarographic wave with a height of 10.8 cm at pH 3.2; when the pH was changed to 7.5 the height of the wave dropped to 5.6 cm. This was in sharp contrast to the ac polarographic behavior of the cadmium ion which was unaffected by similar pH changes.

Lead was used to test the linearity of response of the instrument. Using a supporting electrolyte 1.0 F in potassium nitrate a linear response

was obtained for the wave height for concentrations of lead ranging from 1.0×10^{-2} F to 1.0×10^{-6} F. Figure 5 represents a log-log plot of wave height (measured in scale divisions of chart paper) versus concentration of lead. In obtaining these data, all instrument settings were identical with the exception of the signal level which was varied from a minimum value of 0.001 (for 1.0×10^{-2} F lead) to a maximum value of 1.0 (for 1.0×10^{-6} F lead). All responses were normalized to a signal level of 1.0 before the logs were taken. In addition to verifying the linearity of response of the instrument, the above serves to illustrate its versatility in that relatively concentrated solutions, 1.0×10^{-2} F, and relatively dilute solutions, 1.0×10^{-6} F may be easily determined.

The linearity of response of the instrument was repeatedly checked using a variety of metal ions. However, only lead was examined over such a wide concentration range.

Manganese

It was found necessary for manganese to be present in the +2 oxidation state in order for well defined ac polarographic waves to be obtained.

The best manganese(II) ac waves were obtained with supporting electrolytes of 0.1 F potassium chloride or 0.1 F potassium iodide with the pH adjusted to 7.0. These solutions gave an ac wave with a summit potential of -1.48 volts, a width at half-height of 60 mv (theoretically 45 mv for the two electron reduction to the metal), and a detection limit of about 2×10^{-5} F (1 ppm) manganese. Higher, 1.0 F or lower, 0.01 F, concentrations of either of these salts resulted in broader, less sensitive

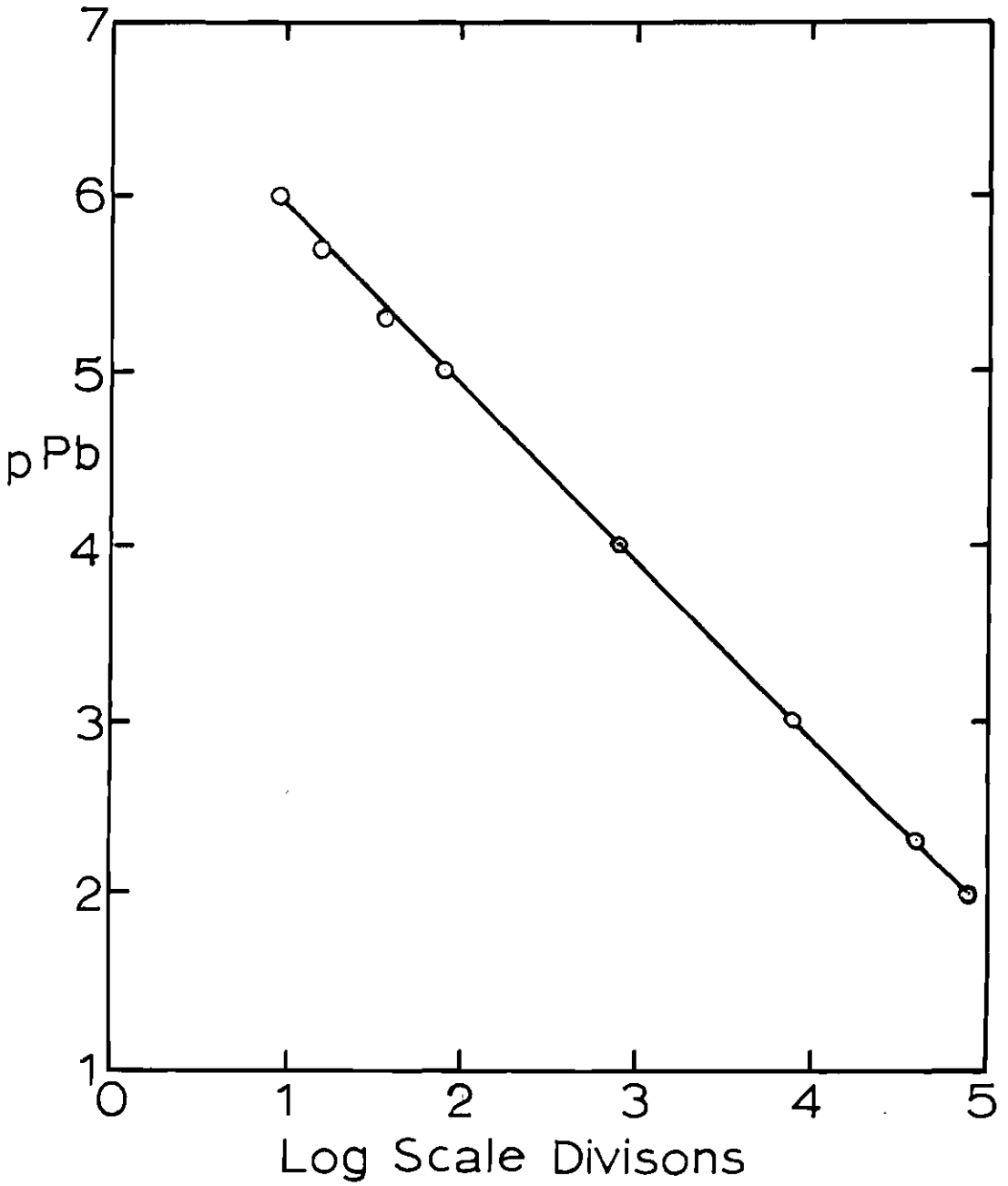

Figure 5. Log-log Plot of Lead Concentration versus Wave Height

waves with uneven baselines. When a solution 0.10 F in potassium nitrate at a pH of 7.0 was used, a wave was obtained comparable to that obtained in potassium chloride or potassium iodide; however, the baseline was uneven. The manganese(II) wave was masked completely by the hydrogen wave at pH values below 5.0.

The supporting electrolytes, potassium cyanide and potassium thiocyanate, were also used. In potassium cyanide, manganese gave a reasonable wave at -1.5 volts with a width at half-height of 70 mv while in potassium thiocyanate a very broad wave with a width at half-height of 140 mv and a summit potential of -1.5 volts was obtained. The detection limits in both of these electrolytes were much less than that found in potassium chloride or potassium iodide.

The use of the hanging mercury drop for the analysis of manganese proved to be unsatisfactory. Stripping techniques using the hanging mercury drop electrode required constant potentials more negative than the -1.5 volts at which manganese is deposited. The drop was very unstable and often fell from the electrode due to the small surface tensions at these very negative potentials (10).

Mercury

The use of a rotating platinum electrode for the determination of the mercury(II) ion was examined. The electrode was the same model described previously in the lead discussion.

The mercury(II) ac wave obtained from the forward (positive to negative) sweep in 1 F potassium nitrate was very poor and erratic. However, stripping analysis using the rotating platinum electrode worked

much better; a very sharp wave, width at half-height 35 mv, was obtained at a summit potential of +0.41 volt in potassium nitrate. The detection limit was about 1×10^{-6} F (0.2 ppm) mercury ion. The deposition of mercury was performed with the electrode rotating and at a potential of +0.2 volt. The results were reproducible providing that proper care was taken to clean the electrode (see below) and that experimental conditions, i.e. plating time, stirring, were strictly controlled. Unfortunately, however, the height of the waves was found not to be linear with the concentration of mercury.

The most effective way of cleaning the electrode has been described by Adams (11). The electrode is first immersed in a chromic acid cleaning solution, whereby a platinum oxide coating forms on the surface. Then the electrode is rinsed with water and treated with a solution of iron(II) in sulfuric acid in order to reduce the platinum oxide to elemental platinum.

Nickel

In no case was a perfectly reversible ac polarographic wave observed for nickel. However, some supporting electrolytes gave reasonably good waves for the reduction of nickel(II) to the metal.

A well defined symmetrical wave was obtained using a supporting electrolyte of 1 F potassium thiocyanate with a summit potential of -0.71 volt. The width at half-height was 65 mv (broad for the two electron change) and the detection limit was about 1×10^{-5} F (0.6 ppm) nickel.

A reasonably good wave was obtained in a solution 1 F in potassium cyanide at a potential of -1.37 volts. The detection limit was about

1×10^{-5} F (0.6 ppm) nickel and the width at half-height was 70 mv (broad for the two electron transfer). The baseline however was uneven.

A supporting electrolyte 0.1 F in potassium nitrate gave a broad wave with a width at half-height of 100 mv at a potential of -1.04 volts. The detection limit was only about 10^{-4} F (6 ppm) nickel. The nickel wave in this electrolyte overlaps with that of zinc.

Frequency studies were conducted on the nickel wave in a supporting electrolyte 1 F in both ammonia and ammonium chloride. At 100 Hz a wave with a width at half-height of 145 mv was obtained at a summit potential of -1.12 volts. At 24 Hz, the wave was narrower, width at half-height of 120 mv (still broad for a two electron change, but an improvement), with a summit potential of -1.06 volts. The behavior of nickel differs from that of the cobalt, on which similar frequency studies were performed (see cobalt discussion), in that there is a shift in the summit potential with frequency. Since both waves are narrower at the lower frequency and the summit potential for nickel is shifted to a more positive value, the separation of the two waves in the ammonia-ammonium chloride medium is much more effective at the lower frequency.

Thallium

Only two supporting electrolytes have been used in the analysis of the thallium(I).

In 1.0 F potassium chloride and 0.85 F potassium hydroxide solutions identical waves are obtained with a summit potential of -0.48 volt, a width at half-height of 90 mv (indicating a perfectly reversible one electron reduction of thallium(I) to the metal), and a detection limit of

about 1×10^{-5} F (2 ppm) thallium. Lead commonly interferes with thallium but the tendency of thallium not to form complexes makes the simultaneous determination of the two metals readily possible since the formation of lead complexes readily shifts the lead waves to more negative potentials (see Chapter IV).

Tin

The ac polarographic behavior of tin proved to be excellent. Tin(IV) gave a symmetrical ac wave at a potential of -0.47 volt in a supporting electrolyte 1 F in hydrochloric acid. The width of the wave at the half-height was 45 mv which corresponds to a reversible two electron reduction. The electrode process that occurred at this potential was the reduction of the tin(II) species to the metal and, in fact, a solution of only tin(II) ions gave a wave identical to tin(IV) in a supporting electrolyte of hydrochloric acid. The tin(IV) was reduced to tin(II) at a more positive potential although this process was totally irreversible and therefore not observed by the ac polarographic technique. If the solution of hydrochloric acid were saturated with sodium chloride the summit potential was shifted to -0.53 volt. The detection limit in hydrochloric acid was about 5×10^{-6} F (0.6 ppm) tin.

A supporting electrolyte 0.5 F in sodium citrate and 1 F in potassium nitrate at a pH of 4.5 shifted the wave for tin(IV) to the more positive potential of -0.13 volt. In this case the tin(IV) ion is reduced to the tin(II) ion which is stabilized by the citrate ion. Because of this stabilization, the tin(IV) to tin(II) reduction gives an observable wave, but the tin(II) (which is strongly complexed with citrate) reduction to

the metal does not. The wave has a width at half-height of 80 mv and a detection limit of about 1×10^{-5} F (1 ppm) tin.

In a supporting electrolyte 1 F in both acetic acid and ammonium acetate tin(IV) gave a well defined wave with a summit potential of -0.6 volt, a width at half-height of 45 mv, and a detection limit of about 1×10^{-5} F (1 ppm) tin.

In a supporting electrolyte of hydrochloric acid the ac polarographic waves of tin and lead coincide.

Vanadium

Only a limited number of results was obtained for vanadium.

In a supporting electrolyte 0.05 F in sulfuric acid a very broad wave, width at half-height of 200 mv, was obtained for vanadium(V) at a summit potential of -0.88 volt. The limit of detection was relatively poor, about 10^{-4} F (5 ppm) vanadium.

The above wave (width at half-height of 200 mv) was obtained using a frequency of 100 Hz. Lowering the frequency to 24 Hz narrowed the wave some (width at half-height of 180 mv) but not enough to improve the results significantly.

Zinc

The ac polarographic reduction of the zinc(II) to the metal was examined in a variety of supporting electrolytes. In particular cases the concentration of the electrolyte proved to have a significant effect on the reversibility of the wave.

The best zinc wave was obtained using supporting electrolytes of 0.01 F potassium nitrate or 0.01 F potassium chloride. In either of

these electrolytes perfectly symmetrical waves were obtained at a summit potential of -1.0 volt. The width of the waves at half-height was 45 mv (corresponding to a two electron reduction) and the detection limit was lower than 1×10^{-6} F (0.06 ppm) zinc.

In supporting electrolytes 0.1 F in potassium salts, i.e. nitrate, chloride, iodide, and thiocyanate, good waves were obtained with the best wave being obtained in a 0.10 F solution of potassium iodide. This is in agreement with results obtained by Randles (12) who studied the effect of the supporting electrolyte on the rate of the reduction of zinc and found that the rate increased in the order nitrate < bromide < thiocyanate < iodide. The concentration of the electrolyte proved to be of more importance, however, since in 0.01 F potassium nitrate the wave for the reduction of zinc was better than in 0.1 F potassium iodide. When the concentration of potassium salts was made 1.0 F much broader waves resulted.

Although better waves were obtained with a potassium salt concentration of 0.01 F, a 0.1 F concentration is recommended for the simultaneous determination of zinc and other metal ions because the background currents are frequently high at potentials removed from the zinc wave when concentrations of 0.01 F are employed.

The hydrogen wave interfered with the determination of zinc when the solutions were too acidic.

When complexed with ammonia zinc gave a wave with a summit potential of -1.4 volts, a width at half-height of 95 mv (indicating irreversibility) and a relatively poor detection limit of 3×10^{-5} F (2 ppm) zinc.

CHAPTER IV

MIXTURES

In this chapter the optimum conditions for the analysis of a number of multicomponent mixtures will be presented. Close attention will be paid to depolarizers that commonly interfere with each other polarographically.

Lead and Cadmium

Although these substances do not normally interfere with each other polarographically, a discussion involving these two metal ions will demonstrate the particular utility of ac polarography in the analysis of one species in the presence of a relatively large amount of another one that is more easily reduced, i.e. reduced at a more positive potential.

A solution 1 F in potassium nitrate was used as the supporting electrolyte. The summit potentials of lead and cadmium in this medium were found to be -0.41 volt and -0.58 volt, respectively. With 2×10^{-5} F cadmium ion a well defined ac wave was obtained; this is not surprising since this concentration is well above the detection limits found for cadmium; however, this concentration of cadmium ion is just barely detectable using classical dc polarography. When a solution that was 1×10^{-3} F in lead and 2×10^{-5} F in cadmium was analyzed, the ac wave for the cadmium was identical to that found in the absence of the lead, although it was, of course, preceded by a large lead wave. A study on the same solutions using dc polarography showed that the large lead step completely

interfered with the determination for this small amount of cadmium.

Cadmium and Indium

The problems associated with the simultaneous polarographic determination of cadmium and indium are well known (13).

In the absence of a suitable complexing agent, the indium(III) is irreversibly reduced at the dme and therefore the ac polarographic determination of cadmium in the presence of indium is relatively straightforward, since reversible ac waves are obtained for cadmium in a variety of supporting electrolytes, both complexing and non-complexing. The reverse situation, i.e., the determination of indium in the presence of cadmium, is not so easily achieved. The two waves were found to be very close together (maximum separation about 30 mv) in a variety of supporting electrolytes; potassium chloride (with and without ethylenediamine), potassium hydrogen phthalate, acetic acid-ammonium acetate, and sodium citrate-potassium nitrate. The simultaneous determination of these two metals in any of these electrolytes would, at best, be very difficult; further, if the concentrations of the two metals were not roughly the same, then such a determination would not be possible.

A supporting electrolyte 0.1 F in potassium iodide was found to be suitable for the simultaneous determination of cadmium and indium, with a separation of 0.12 volt between the two summit potentials (E_s for indium -0.54 volt, E_s for cadmium -0.66 volt).

A frequency of 24 Hz was found to be better than 100 Hz for this determination. At low indium ion concentrations (below 1×10^{-5} F) the dissolution of mercury interfered with the determination of indium at a

frequency of 100 Hz; whereas, this interference did not occur at a frequency of 24 Hz. Also the resolution of the two waves was better at 24 Hz. At higher concentrations of potassium iodide, e.g. 1 F, the wave due to the dissolution of mercury interfered with the determination of small amounts of indium regardless of the frequency employed.

Zinc and Manganese

A solution 0.1 F in potassium iodide proved to be an excellent supporting electrolyte for the simultaneous determination of zinc, E_s = -0.98 volt, and manganese, E_s = -1.48 volts. Although a solution of 0.01 F potassium iodide gave a slightly better ac wave for zinc, background currents at potentials corresponding to waves of other depolarizers, e.g. cadmium, manganese, were high. For this reason, and because iodide is the best of the potassium salts for the determination of zinc, a 0.1 F solution of potassium iodide is recommended for the determination of zinc and manganese. It is obvious that this supporting electrolyte would be well suited for the simultaneous determination of indium, E_s = -0.54 volt, cadmium, E_s = -0.66 volt, zinc, E_s = -0.98 volt, and manganese, E_s = -1.48 volts.

Lead, Tin, and Thallium

In acidic halide solutions the waves of thallium and tin coincide with that of lead. In 0.5 F hydrochloric acid the summit potentials are -0.49, -0.47, and -0.43 volt, respectively. The tin wave does not occur however in a non-complexing medium such as potassium nitrate, but the thallium and lead waves do and still coincide.

Thallium and lead may be simultaneously determined in 0.85 F

potassium hydroxide. The resolution of the two waves in this electrolyte was found to be complete with a separation of 0.27 volt being obtained; E_s for lead -0.76 volt, E_s for thallium -0.49 volt. Tin is polarographically inactive in this medium.

In potassium hydroxide, cadmium is polarographically inactive and, therefore, does not hinder the determination of thallium and lead. However, the simultaneous determination of thallium, lead, and cadmium was found to be possible by using a solution of 0.1 F potassium nitrate in a solution made 0.6 percent ethylenediamine. The summit potentials were -0.48 for thallium, -0.68 volt for lead, and -0.86 volt for cadmium. Tin is polarographically inactive in this medium.

While there are many supporting electrolytes in which lead may be determined in the presence of tin, the opposite situation, i.e., the determination of tin in the presence of lead is not so readily possible. Two electrolytes suitable for the simultaneous determination of these two metals were used in this study. In a solution 0.5 F in sodium citrate 1 F in potassium nitrate and of pH 4.5, tin(IV) gave a reasonably well defined wave at a summit potential of -0.13 volt; while the lead wave had a summit potential of -0.53 volt. In a solution 1.0 F in both acetic acid and ammonium acetate well defined, reversible waves for lead and tin were obtained at -0.48 volt and -0.60 volt, respectively. Although the tin behavior is more reversible in the acetate medium than in the citrate medium, the citrate offers a greater separation of the two waves. Lead shows reversible behavior in both electrolytes. Cadmium interferes with the determination of tin in the acetate medium. Iron and copper interfere in the citrate medium. Copper, tin, and cadmium may simultaneously be determined in 0.5

F hydrochloric acid. This is of a particular importance since cadmium and copper frequently occur in actual samples.

Bismuth and Antimony

A solution 0.5 F in hydrochloric acid would, in most cases, serve as a suitable supporting electrolyte for the simultaneous determination of bismuth and antimony; E_s for bismuth of -0.065 volt, E_s for antimony of -0.14 volt (a separation of 0.075 volt). However, as mentioned in the discussion on bismuth (see Chapter III), a 0.5 F sodium succinate solution offers a much greater separation, 0.41 volt, between the two waves. Sodium succinate would be very well suited for the analysis of small amounts of antimony in the presence of large amounts of bismuth.

Nickel and Cobalt

For the simultaneous determination of nickel (E_s = -0.71 volt) and cobalt (E_s = -1.1 volts) 1.0 F potassium thiocyanate was found to be a suitable supporting electrolyte.

A solution 1 F in both ammonia and ammonium chloride also proved to be suitable for the simultaneous determination of nickel and cobalt. The resolution of the two waves was much better at 24 Hz than at 100 Hz (see nickel, Chapter III).

CHAPTER V

SURFACTANTS

Small amounts of surfactants (surface-active substances) are often used in conventional dc polarography to supress maxima on the steps. If these maxima are not eliminated the analysis of metal ions using the dc technique is seriously hindered. In ac polarography, however, the presence of surfactants must usually be avoided because the rate of the electron-transfer reaction is markedly decreased and a large decrease in, or even disappearance of, the ac polarographic wave may occur. This chapter deals with the effect of the presence of various types of surfactants on the ac polarographic method, and with elimination of interferences caused by this presence.

Nonionic Surfactants

The effect of uncharged surfactants, e.g. Triton X-100, will generally lead to irreversible dc polarographic behavior and, therefore, a broadening or disappearance of ac polarographic waves. This behavior has been verified in this laboratory using the surfactants n-amyl alcohol, octyl alcohol, and Triton X-100.

The presence of n-amyl alcohol or octyl alcohol caused a 1×10^{-3} F lead solution in 1 F potassium nitrate to give an irreversible dc step. The ac wave broadened and a significant loss in wave height was observed. A solution (2×10^{-5} F cadmium in potassium nitrate) which gave a well defined reversible ac wave which was completely suppressed upon the

addition of n-amyl or octyl alcohol.

Triton X-100, when added to a solution 1×10^{-5} F in cadmium, 4×10^{-5} F in zinc and 1 F in potassium nitrate at pH values ranging from 1.5 to 3.7, completely suppressed the cadmium and zinc ac waves. In a solution 2.5 F in perchloric acid, 1×10^{-5} F in lead, and 1×10^{-5} F in cadmium, the presence of Triton X-100 causes broadening of the lead wave and total disappearance of the cadmium wave.

In all cases, the solutions were saturated with the surfactant. Clearly, the presence of this type of surfactant cannot be tolerated when using the ac technique. A procedure for the elimination of interferences caused by the presence of surfactants is given below (see Chapter VI).

Ionic Surfactants

Several investigators have examined the effect of ionic surfactants on dc polarographic waves (14,15,16). Generally, results have indicated that systems in which the surfactant has a charge opposite in sign to that of the depolarizer yield a wave corresponding to a reversible reduction of the depolarizer; whereas, systems examined in which the charge of the surfactant and the depolarizer were of the same sign have irreversible waves. These phenomena have been interpreted by assuming that the depolarizer can penetrate through certain surface films (14,15), or that the formation of a bridge accelerates the electron-transfer between the electrode and the depolarizing species (17). The irreversible waves can probably best be explained by an electrostatic repulsion involving the electrode and the depolarizer.

More recently, Jacobsen (18) and Jacobsen and Gundersen (19) have

reported results in which well defined ac waves were obtained in the presence of charged surfactants, providing that the charges of the surfactants were of signs opposite to those of the depolarizers. Since the reduction is brought about by an electron-transfer through an absorbed layer, Jacobsen has proposed to call these waves "ac penetration waves" (18). These waves were not observed with the depolarizers and the surfactant having the same charge sign. This observation is in agreement with results previously cited in which irreversible dc waves are obtained under these conditions. The height of the ac penetration wave was found to be proportional to the bulk concentration of the depolarizer (18).

Since ac penetration waves are observed under appropriate conditions it is obvious that the presence of ionic surfactants may sometimes be tolerated and, in fact, may be analytically useful. Recently Jacobsen and Tandberg (20) have reported results in which the anionic surfactant Benax was used in the determination of cadmium in the presence of large amounts of indium. In this case, the anionic surfactant served as an electrochemical masking agent for the negatively charged indium citrate complexes but did not affect ac polarograms of uncomplexed cadmium ions.

The effect of commercial detergents, Tide X-K, Comet, and Alconox, was examined. The anionic species sodium dodecylsulphate (SDS) is the surface-active substance present in these detergents. When added to a solution 1×10^{-5} F in lead, 1×10^{-5} F in cadmium, and 4×10^{-5} F in zinc and 1 F in potassium nitrate, at a pH of seven or greater, the waves of all three depolarizers were depressed. However, when the pH was lowered to values below 4.5, the ac waves were unaffected. When similar studies were performed using pure SDS, identical results were obtained, i.e.,

simple acidification of the solution was adequate to eliminate the interference due to the surfactant. The concentration of the surfactant in the polarographic solutions was 0.1 gram per liter in all cases.

In this case, the surfactant, SDS, is negatively charged and the depolarizers, lead, cadmium, and zinc are positively charged since a non-complexing supporting electrolyte is used. It is not surprising, therefore, that an ac penetration wave was observed under these conditions.

Studies involving the positive surfactants, Onyx and Armeen, also indicated the importance of the charge of the depolarizers and the surfactants. Onyx and Armeen are long-chain molecules and have active amine groups that take up protons (and thereby become positive) as the acidity of their solutions increases.

When Onyx was added to a solution 1×10^{-5} F in cadmium and 4×10^{-5} F in zinc and 1 F in potassium nitrate, which leaves both species present as essentially M^{2+} ions, the ac wave heights of both metals were lowered. As the pH was lowered from an initial value of about five, both waves became more depressed, with a complete disappearance of the waves occurring at a pH of about two. Since the depolarizers and the surfactant are positively charged, the depolarizers are probably electrostatically repelled from the adsorbed layer and no ac wave is observed.

Similar results were found in a study involving Armeen in which 2×10^{-5} F lead and 2×10^{-5} F cadmium in a supporting electrolyte of 0.5 F perchloric acid was used. Upon addition of Armeen to this solution, both the lead and cadmium waves were completely suppressed. Since perchloric acid is non-complexing, the depolarizers are again present as M^{2+} and since these are repelled at the electrode surface by the positive

surfactant a reversible reduction is not possible.

The situation changes significantly, however, when the solution is made 0.2 F in sodium chloride. Well defined waves are obtained for lead and cadmium in this medium even when Armeen is added to the solution; in fact, there is a slight gain in wave height due to the presence of Armeen. In this case the ions are now present predominantly as the complexes MCl_2 and MCl_3^-. These are able to pass through the adsorbed positive layer and their reduction is not hindered. The height of the lead wave was found to be linear with the concentration of lead ions; this linear relationship did, however, not apply to the cadmium ion.

Similar results were obtained for the positive surfactant Onyx when added to a lead and cadmium containing solution of 0.5 F perchloric acid-0.2 F sodium chloride. The lead and cadmium waves were found to be unaffected by the addition of Onyx.

In the above studies, all of the polarographic solutions were saturated with Onyx and Triton X-100.

CHAPTER VI

ACTUAL SAMPLES

A variety of samples, all of which were obtained from the Atlanta area, was examined. This chapter outlines the results obtained and presents a general procedure for analysis.

Initially, actual samples, i.e. natural water samples and industrial samples, were analyzed directly without any pretreatment. As the studies progressed, it was found expedient to develop a general procedure for the removal of interfering organic materials. The use of this procedure assured that any organic species that might interfere with the ac polarographic method would be obviated and that any metal ions present at detectable limits could be determined.

Since the optimum conditions for the analysis of individual metals (Chapter III) and mixtures (Chapter IV) have already been presented, only the results obtained will be presented here.

Some samples were initially analyzed without pretreatment, i.e. the supporting electrolyte was added directly to the sample, the resulting solution was deaerated with nitrogen and the ac polarogram recorded. When the presence of metal ions was indicated, the concentrations were determined by the method of standard addition. In many cases standard additions of metal ions, not detected in the sample, were made to determine whether their determination would be feasible if present. The results obtained from the studies without pretreatment must necessarily be viewed

with some skepticism due to the possible presence of interfering surfactants.

Since the presence of surfactants is known to interfere with the ac polarographic method (see Chapter V), it was deemed necessary to establish a pretreatment procedure to eliminate their presence. This was accomplished by evaporating the solutions in the presence of perchloric and nitric acids. All evaporations were carried out in an Erlenmeyer flask using a hot plate under a hood.

The use of perchloric and nitric acids for the elimination of organic matter is well known (21) and has recently been described for the elimination of surface active compounds in the determination of lead ions by square-wave polarography (22).

Perchloric acid alone was found to be insufficient for the destruction of surfactants. When concentrated perchloric acid was added to a saturated aqueous solution of Triton X-100, a black, tarry substance formed as the evaporation proceeded. This substance persisted, even upon prolonged heating. When concentrated nitric acid was added and the heating continued, the black substance slowly disappeared giving rise to the characteristic white fumes of perchloric acid.

The uncharged surfactant, Triton X-100, was chosen to test the effectiveness of the method since even trace concentrations of Triton X-100 are known to severely interfere with ac waves, when a solution containing 1×10^{-5} F lead, 1×10^{-5} F cadmium, and saturated with Triton X-100 was treated with concentrated perchloric and concentrated nitric acids followed by evaporation to fumes of perchloric acid, the ac polarographic interference due to the presence of Triton X-100 was eliminated.

Considering the difficulties that are encountered when surfactants

are present and the fact that an evaporation treatment with a perchloric acid-nitric acid solution will eliminate these difficulties, it was possible to develop the following procedure with the most practical approach for the ac method. The evaporation of the relatively large volume used (about 300 ml) serves to concentrate any metal ions present and thereby bring them to a detectable limit; this may consist of as much as a ten-fold concentration step.

Procedure

1. Into a 500 ml Erlenmeyer flask, introduce a known volume (between 250 and 300 ml) of sample solution.

2. Add 25 ml each of reagent grade concentrated perchloric and concentrated nitric acids.

3. Evaporate on a hot plate to the white fumes of perchloric acid (to about 25 ml) under a hood.

4. Remove the flask from the hot plate and cool.

5. Transfer the resulting solution quantitatively to a graduated polarographic cell, add an appropriate amount of sodium chloride to make the final solution 0.2 F in sodium chloride, and bring to a known volume (between 25 and 50 ml is convenient). If desirable, a pH adjustment may be performed before bringing the solution to final volume.

6. Deaerate with nitrogen and record the ac polarogram.

The procedure requires about four or five hours for completion. If the large volume is not necessary, that is, if the concentration step is not necessary, then the pretreatment procedure requires considerably less time (about one hour). Once the white fumes of perchloric acid appear all organic matter has been eliminated. If desirable, further evaporation serves to remove any unwanted perchloric acid.

Discussion and Results

The results obtained, using the method described herein, in the analysis of actual samples were not compared to those of another analytical method. It was felt that such a comparison was not necessary due to favorable results obtained when a variety of artificial samples was analyzed. In the analysis of the artificial samples the problems encountered in actual samples were dealt with. In all cases, the presence of possible interferences, such as high salt concentrations or surfactants, proved to either not interfere (as was the case with high salt concentrations), or could be readily eliminated (as was the case with surfactants). In addition, comparison studies would be difficult to achieve, since any other method comparable in sensitivity and speed to the method herein described would be difficult to realize.

The application of the ac polarographic method, both with and without the perchloric acid-nitric acid pretreatment, gave the following results. In some cases, only relatively small volumes of sample were available; when sufficient sample was available, 250 ml were used when the perchloric acid-nitric acid pretreatment procedure was employed. In all cases the final polarographic determination was performed on 50 ml of solution. First, results obtained on natural water samples will be presented followed by results obtained when industrial samples were analyzed.

In the analysis of a sample obtained from the Chattahoochee River at Paces Ferry Road, no metals were found within the detection limits of the instrument. When standard additions of iron, thallium, and lead were made, well defined waves resulted.

Analysis of a sample obtained from Sope Creek at Paper Mill Road

showed no detectable metal ions. Standard additions of lead, cadmium, and zinc resulted in well defined waves.

When a sample obtained at the foot of the Allatoona Dam was analyzed no detectable metals were found. The standard addition of manganese resulted in a well defined wave.

In the analysis of a sample obtained at the foot of Buford Dam, no metals were found to be present at concentrations greater than the detection limits of the instrument.

A sample obtained from Rottenwood Creek gave some interesting results. Using a supporting electrolyte 1.0 F in potassium chloride and without the perchloric acid-nitric acid pretreatment, standard additions of lead, cadmium, zinc, and manganese resulted in well defined waves. However, the heights of these waves did not increase in a linear fashion with increasing concentration. This problem was eliminated by employing a strongly acidic supporting electrolyte (0.5 F hydrochloric acid) in which linear responses were obtained for standard additions of cadmium and lead. Apparently, this strong acid solution served to eliminate some interference. Since the Rottenwood Creek sample appeared to contain some interfering species, the possibility of metals being present that could not be detected due to an interference was suspected. However, when the perchloric acid-nitric acid pretreatment procedure was applied to 110 ml of the Rottenwood Creek sample no metals were found.

The analysis, without pretreatment, of a sample obtained from the Chastain Park Lake gave an iron concentration of 9×10^{-6} F (0.5 ppm). Standard additions of copper, tin, lead, cadmium, zinc, and manganese resulted in well defined ac waves. The perchloric acid-nitric acid pre-

treatment procedure was not applied to this sample.

The appearance of a sample obtained from the South River suggested that a rather high concentration of soaps and detergents might be present, and therefore, possible interference by surfactants was suspected. However, well defined ac waves with heights linearly proportional to metal ion concentrations were obtained upon the standard additions of antimony, tin, and cadmium. The sample was found to contain iron in a concentration of 2×10^{-6} F (1 ppm); no other metals were found. The pretreatment procedure was not applied to this sample.

In addition to the natural water samples outlined above, some samples common to industrial processes were obtained and analyzed.

A sample of effluent which is normally discharged directly into the Flint River was obtained from the Delta Airlines Plating facility in Atlanta. This sample was found to contain small concentrations of metals. When the sample was analyzed without pretreatment, concentrations of 5×10^{-7} F (0.06 ppm) cadmium, 7×10^{-6} F (0.4 ppm) nickel, and 1×10^{-5} F (0.6 ppm) iron were found. All of these concentrations are very close to the detection limit of the method. Standard additions of lead and zinc resulted in well defined waves. When the perchloric acid-nitric acid pretreatment procedure was applied to this sample the following results were obtained. Two hundred and fifty ml of sample were used and the final volume in the polarographic cell was 50 ml; this represents a fivefold concentration step. The ac polarograms obtained from the cell solution gave results of 3×10^{-6} F cadmium, 2×10^{-6} F lead, and 7×10^{-6} F copper; this corresponds to 6×10^{-7} F (0.07 ppm), 4×10^{-7} F (0.08 ppm), and 1×10^{-6} (0.06 ppm) cadmium, lead, and copper, respectively, in the

original 250 ml of sample. Of these metals, only cadmium was found when ac polarograms were recorded on the sample without the concentration step. Nickel and iron were not analyzed for following the pretreatment procedure since they are both polarographically inactive in the resulting solution.

When an industrial waste sample, also obtained from Delta, was analyzed without pretreatment, a copper concentration of 9×10^{-6} F (0.6 ppm) was found. The application of the pretreatment procedure using 250 ml of sample and a final volume in the polarographic cell of 50 ml, again a fivefold concentration step, gave the following results. Concentrations of 3×10^{-6} F cadmium, 1×10^{-6} F lead, and 2×10^{-5} F copper were found in the 50 ml cell solutions; this corresponds to concentrations of 6×10^{-7} (0.07 ppm) cadmium, 2×10^{-7} (0.04 ppm) lead, and 4×10^{-6} F (0.2 ppm) copper in the original 250 ml of sample. Only copper was found when ac polarograms were recorded without the pretreatment concentration step.

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*Abbreviations used herein follow the form employed by Chemical Abstracts.

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VITA

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